





MONOGRAPH No. II  
NATIONAL RESEARCH COUNCIL  
COMMITTEE ON ELECTRICAL INSULATION  
J. B. WHITEHEAD, CHAIRMAN  
THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.

# LIQUID DIELECTRICS

Monographs published under the auspices of  
the Committee on Electrical Insulation  
Division of Engineering and Industrial Research  
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# LIQUID DIELECTRICS

BY

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*WITH 59 FIGURES IN TEXT*

NEW YORK  
JOHN WILEY & SONS, INC.  
LONDON: CHAPMAN & HALL, LIMITED

1933

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## FOREWORD

THIS volume is the second of a series of monographs published under the auspices of the Committee on Electrical Insulation of the Division of Engineering and Industrial Research, National Research Council. It is very fitting that the first, Professor Loeb's interesting volume, "The Nature of a Gas," should be followed by one presenting a survey of the theory of liquid dielectrics and of their properties as insulators.

In many respects the liquids are the most interesting among dielectric materials. They have excellent insulating characteristics and are widely used in commercial insulation, and their limitations are of the first importance to the electrical engineer. They are, however, highly anomalous, showing many departures from classical laws. On the other hand, the relative ease with which they may be handled, and the wide ranges of variation of physical properties which they offer, render them especially attractive to the scientific investigator. Drawing upon his extensive experience as research engineer and physicist, Dr. Gemant gives us a much-needed correlative survey of the general physics of liquids as related especially to their behavior as dielectrics and insulators. The Committee acknowledges with appreciation its indebtedness to Dr. Gemant and presents this volume with confidence.

The thanks of the Committee are extended particularly to Professor V. Karapetoff, Chairman of the Sub-committee on Physics, who voluntarily undertook the exacting task of translation of Dr. Gemant's manuscript. The reader will find easy going and faithful presentation of the author's text. The Committee also gratefully acknowledges the

generous financial assistance accorded by The Detroit Edison Company through its President, Alex Dow, and its Chief of Research, C. F. Hirshfeld, in the preparation for publication of the manuscripts of this and the preceding monograph.

J. B. WHITEHEAD, *Chairman.*

THE JOHNS HOPKINS UNIVERSITY  
April 27, 1933

## AUTHOR'S PREFACE

I AM happy to respond to the friendly request of the Editor of this series, to write a monograph on Liquid Dielectrics.

I have kept in mind mainly the needs of electrical engineers. Accordingly, although the whole domain of the physics of liquids is touched upon, the choice of the particular topics has been guided by the specific purpose in view. Only those mechanical, thermal, and physico-chemical properties of liquids have been included which are of interest in dielectric behavior. For the same reason, the electrical and electro-optical sections of the book are the more complete; the method of treatment is often only descriptive, and on many points not so important for the engineer it is even kept rather sketchy. For the clearer understanding of such a reader the more rigorous discussions and mathematical deductions have been made as few as possible. A brief outline of the most important practical applications in electrical engineering is given at the end.

In the preparation of the text I have used in many places the results of my own investigations, which in part were conducted in the cable factory of the Siemens-Schuckert Cable Works, Berlin.

A brief bibliography, arranged according to the sections of the book, is appended; in addition to a few reference works it contains some articles selected from the literature of the last few years.

I am greatly indebted to Professor Vladimir Karapetoff for his careful translation of the German text, and to Professor J. B. Whitehead for his co-operation in supervising the editing of this work.

A. GEMANT

BERLIN, GERMANY  
June, 1933



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7.2° A for lead, the resistance suddenly drops down almost to zero. In such a metal a current continues to flow for a long time after the voltage has been removed and disappears at an exceedingly low rate.

Next come the metals at ordinary temperatures, with values of resistivity between  $10^{-6}$  and  $10^{-5}$  ohm cm. Then follow carbon with  $10^{-2}$  ohm cm and aqueous solutions of electrolytes with resistivities of 1 to  $10^5$  ohm cm. Electrolytic solutes in organic solvents possess resistivities of  $10^3$  to  $10^{12}$  ohm cm; the resistivity of slate is  $10^8$ , of marble  $10^{10}$ , of glass  $10^{14}$ , of mineral oils  $10^{15}$ , of sealing-wax  $10^{16}$ , of hard rubber  $10^{18}$  ohm cm, etc. Of all known insulating materials, paraffin, amber, and fused quartz possess the highest resistivity.

At the end of this series may be placed gases, for which the resistivity at normal pressures is practically infinitely high; in this respect they are the opposites of metals in the super-conducting state. We also see that there is a fairly continuous series of materials which together comprise all the possible values of resistivity. For practical purposes this whole range may be divided into three parts. The range with resistivities from 0 to  $10^6$  ohm cm comprises the conductors, the range of  $10^6$  to  $10^{12}$  ohm cm comprises semi-conductors, and the range from  $10^{12}$  to  $\infty$  the non-conductors. Thus we have three principal divisions, although the indicated limits are only approximate and overlap each other, so that the foregoing divisions should not be taken as representing exact quantitative data. Generally speaking, the concept of dielectrics comprises both the non-conductors and the semi-conductors. One may speak of perfectly-insulating dielectrics and slightly-conducting dielectrics. The foregoing description and definition give a fair idea of the present situation in this field.

Although the value of resistivity is best adapted to characterize a substance, because according to its value a substance may serve as an insulator or not, the picture is



not complete unless one also knows the value of the dielectric constant. The latter term indicates the property of an insulating material, when used in a condenser, to increase the capacitance, compared to that of a vacuum. If the capacitance does not increase, the dielectric constant is said to be equal to 1. For known substances the dielectric constant has values up to 100; for certain colloidal solutions even higher values have been measured. Of course, metals are not considered here, as they are used for the condenser plates, so that the intervening space must be filled with a substance of lower conductivity, in order to maintain an appreciable difference of potential across the condenser. Thus the series of materials for filling condensers begins with aqueous solutions and may be extended to all such substances whose resistivity is of an order of magnitude greater than 1 ohm cm.

There is a noteworthy relation between the values of resistivity and dielectric constant of various substances, so that if these values be written in two parallel columns the values of dielectric constant decrease with the decreasing values of conductivity. The reason for this parallelism will be discussed at the end of Section 9. Here we wish merely to call attention to this double "dielectric series." Aqueous solutions have a dielectric constant of about 80. Since they belong to the conductor class they are of no interest to us in this discussion. Beginning with substances whose resistivity is about  $10^6$  ohm cm, the values of the dielectric constant are of the order of magnitude of 20 to 30. Thus dielectrics may be characterized as substances whose dielectric constant is between 1 and about 30. Substances whose dielectric constant lies between 30 and about 6 constitute semi-conducting dielectrics; those between 6 and 1 are insulating dielectrics.

The foregoing ranges of the values of resistivity  $\rho$  and dielectric constant  $\epsilon$  are shown schematically in the following table, although the relationship between  $\rho$  and  $\epsilon$  should not be considered a strictly functional one.

The upper row gives values of resistivity  $\rho$  in ohm centimeters, and the lower row those of the dielectric constant  $\epsilon$ . The scale of divisions is a logarithmic one. The classification into conductors and dielectrics is indicated below the rows of figures. It is of importance to consider both  $\rho$  and  $\epsilon$  from a theoretical as well as a practical point of view, because it is not always feasible for both quantities to be measured. Consequently with one measurement of either  $\rho$  or  $\epsilon$ , one may often decide in which of the three foregoing groups a given substance belongs.

$\rho$	$10^{-5}$	1	$10^5$	$10^{10}$	$10^{15}$	$10^{20}$
$\epsilon$	80		20	6	3	2
Conductors			Dielectrics		Insulators	
			Semi-conductors			

The foregoing considerations will now be applied to liquids, the subject of this monograph. As indicated above, we exclude aqueous solutions as belonging to conductors. Ordinary distilled water has a resistivity of  $10^5$  ohm cm and lies therefore on the boundary line between conductors and semi-conductors.

Looking over the list of inorganic liquids one has to exclude hydrocyanic acid, with its dielectric constant of 95. A number of inorganic substances may be designated as dielectrics, although only a few are used in practice.

1. Some elements are good dielectrics in their liquid state. For liquid sulfur in the vicinity of the boiling point,  $\epsilon = 3.4$ ; for liquid phosphorus at  $45^\circ \text{C}$ ,  $\epsilon \approx 3.8$ ; and for bromine  $\epsilon = 3.2$  at  $23^\circ \text{C}$ . In practice only sulfur is used, of course in the solid form.

2. Halogen compounds of some elements are semi-conductors in the liquid form. For example, for phosphorus trichloride,  $\epsilon = 4.7$  at  $22^\circ \text{C}$ ; for arsenic trichloride,  $\epsilon = 12.6$  at  $17^\circ \text{C}$ ; for tetrachloride of tin,  $\epsilon = 3.2$  at  $22^\circ \text{C}$ , etc. Carbon disulfide is a good insulator with  $\epsilon = 2.6$ .

3. There are inorganic gases which may be liquefied at a low temperature or at high pressure. For oxygen,  $\epsilon = 1.5$  at  $-182^\circ \text{C}$ ; for liquid air,  $\epsilon = 1.43$  at the boiling point under atmospheric pressure. For chlorine,  $\epsilon = 1.97$  at  $0^\circ \text{C}$ ; and for carbon dioxide,  $\epsilon = 1.52$  at  $15^\circ \text{C}$ . This group of substances is at present of theoretical interest only.

Of much more importance are organic liquid dielectrics. From the point of view of practicality, one may even say that all liquid dielectrics are organic substances. This is to be regretted, since inorganic compounds, generally speaking, are more stable than organic. The substances in Group 3 above seem to be the most promising for the future. For example, carbon dioxide should be an excellent insulating material at  $15^\circ \text{C}$  and at a pressure of 52 atmospheres. In proportion as pressure-resisting condensers find a more extensive field of application, this group of insulating materials will become of greater practical importance. However, at the present time the organic liquids are almost the only ones used in practice.

We shall briefly review some organic compounds. The most important group is that of hydrocarbons, which are substances consisting of carbon and hydrogen only. All of them have a low conductivity and a low dielectric constant. Chemically they are very inactive because they contain no oxygen or nitrogen and therefore do not attack other substances, such as metals. Saturated hydrocarbons, that is, those which have no double bond, are very stable and difficult to modify by various chemical or physical agents. (See Section 7.) According to their molecular structure they may be subdivided into open-chain and ring compounds. Hexane ( $\epsilon = 1.88$  at  $17^\circ \text{C}$ ) is an example of a compound which belongs to the open-chain or aliphatic

group. An important example of the ring type or cyclic structure is benzene ( $\epsilon = 2.29$  at  $18^\circ \text{C}$ ), whose molecule has a single carbon ring.

Hydrocarbons may be divided into two groups on another basis also, namely, into those which are chemically definite compounds and those which are mixtures of substances not exactly known. Hexane and benzene belong to the first group. From the practical point of view the mixtures are much more important, although it is only approximately known of what components they consist. There is an infinite number of such products, from the thinnest to the most viscous liquids. Petroleum ether ( $\epsilon = 1.8$ ) is an example of a thin liquid. Kerosene oil ( $\epsilon = 2.1$ ) is of medium viscosity, and then follow paraffin oil ( $\epsilon = 2.1$ ) and transformer oil ( $\epsilon = 2.2$ ). This series may be continued to cylinder oils and the various vaselines; paraffin and ozokerite are usually counted with solids, although strictly speaking they are highly viscous liquids.

The group of substances known as transformer oils and cylinder oils will be considered under the name of mineral oils. Hydrocarbons belonging to the aliphatic series (oils with a paraffin base) constitute more than two-thirds of the bulk of Pennsylvania oils, whereas cyclic hydrocarbons, mostly those with more than one carbon ring (oils with a naphthene base), constitute more than two-thirds of the bulk of Texas oils and Russian oils.

The foregoing résumé comprises the most essential insulating liquids used in engineering practice, and it remains only to mention a few other organic liquids. Halogen substitution products are partly semi-conductors, partly insulating materials. Compounds like allyl chloride ( $\epsilon = 8.2$ ) can hardly find a practical application. Generally speaking, organic compounds with double bonds are not so suitable for technical purposes, because of their instability. On the other hand, saturated hydrocarbons with chlorine substitution, as for example chloroform ( $\epsilon = 5.2$ ) and particularly carbon tetrachloride ( $\epsilon = 2.2$ ), are suitable for

some purposes. The latter in particular is chemically rather inert and also possesses the valuable property of being non-inflammable; because of this it is also used for fire-extinguishing.\*

Hydroxyl substitution products, that is, alcohols, are different in that they all have a relatively high dielectric constant and a high conductivity. Methyl alcohol and ethyl alcohol ( $\epsilon = 31.2$  and  $\epsilon = 25.8$ ) are on the border line between conductors and semi-conductors; certain alcoholic solutions of electrolytes are decidedly conductors of electricity. Alcohols are valuable as additions to good insulating liquids in small quantities. By their use the conductivity of an insulating material may be increased to a certain degree, which is often desirable. Phenol, which may be considered as the alcohol of benzene, has similar properties and is also sometimes used as an ingredient in insulating compounds.

Those organic compounds which contain oxygen atoms in the middle of their molecule, that is, the ethers and the ketones, behave similarly to the alcohols. We shall later consider the cause of the phenomenon that the presence of oxygen considerably increases the values of the dielectric constant and of the conductivity; here we merely wish to call attention to this fact. Ethyl ether ( $\epsilon = 4.3$ ) and acetone ( $\epsilon = 21.5$ ) may be mentioned as typical representatives of these groups. Nitro- or amino-compounds also belong among semi-conductors, for example, nitrobenzene ( $\epsilon = 36.5$ ); besides, they are somewhat active chemically. Nitrobenzene is likewise suitable as an admixture because of its high dielectric constant, when it is desired to increase the permittivity of an insulating compound. It is also used in the Kerr cell (see Section 18).]

Aldehydes and acids are still better conductors of electricity. Also, acids become electrolytically dissociated

\* Under some conditions, however, carbon tetrachloride may be extremely reactive. For this reason it has not been used to any extent in good electrical design.—Translator.

and therefore cannot be considered under dielectrics: for example, acetic acid with  $\epsilon = 9.7$ . Moreover, such compounds are difficult to obtain completely free from water; they usually mix with water in any proportion, whereby their conductivity is increased still more. With a high water content they can no longer be considered organic liquids, but rather they are aqueous solutions of organic electrolytes.

Esters, compounds formed by an interaction of acids with alcohols, include another group of technically important insulating substances, the vegetable oils. Esters obtained from monovalent alcohols are not suitable for our purposes (for example, ethyl acetate with  $\epsilon = 6.1$ ), but those obtained from the trivalent glycerin with acids of higher molecular weight are valuable. Among others may be mentioned olive oil ( $\epsilon = 3.1$ ), linseed oil ( $\epsilon = 3.3$ ), almond oil ( $\epsilon = 2.8$ ), and castor oil ( $\epsilon = 4.6$ ). The last substance in particular occupies an exceptional position among insulating liquids because no other in practical use possesses such a high dielectric constant. It is therefore often used in scientific research work. In spite of their relatively high oxygen content, compounds of this group are suitable for insulation purposes because of their high molecular weight, high boiling point, and chemically closed molecular structure. Tricresyl phosphate, which is an excellent medium in breakdown tests of solids, may also be mentioned.

After this general review of the various chemical groups of dielectrics a few words may be added about their mutual miscibility. Often the characteristics required of a dielectric may be obtained by artificially mixing two substances. But not all desired mixtures may be obtained at will, because often the miscibility of two substances is quite low. It is therefore advisable to keep the following two fundamental relationships in mind.

1. Two liquids are the more miscible the nearer to each other they are in the above-mentioned dielectric series.

By comparing their resistivities or their dielectric constants one may roughly predict whether two substances picked out at random are miscible within wide limits. This law has its limitations, because other factors enter into the question of miscibility. For example, ethyl alcohol is just as far in the series from transformer oil as from benzene, yet it is not miscible with transformer oil although it forms mixtures with benzene in any desired proportion.

2. Two non-miscible liquids may be mixed to some extent through the intermediary of a third liquid which is miscible with both. For example, if it is desired to add some ethyl alcohol to a transformer oil in order to increase its conductivity, this can be done by means of benzene, which is miscible with both. One can dissolve much more alcohol in a mixture of 10% benzene and 90% transformer oil than in pure oil alone. This method is often used to advantage.

*Summary.*—All substances, and particularly all liquids, may be arranged in a dielectric series, according to their increasing resistivity and diminishing dielectric constant, which two characteristics usually go hand in hand. The farther to the right a liquid is in this series, the better insulating material it produces. The ideal to be reached is to establish definite relationships between the chemical constitution and the above-mentioned series so that one may predict the dielectric properties of a compound from its chemical structure. This end has not yet been achieved, although a few chemical indications in this direction may be given. An understanding of such relationships will be made more clear and detailed through an analysis of the individual properties of dielectrics in the following sections of the book.

## CHAPTER II

### ESSENTIAL MECHANICAL AND THERMAL PROPERTIES

**2. Capillarity.**—We shall begin with a discussion of the so-called capillary phenomena because in some respects they are fundamental to the understanding of liquids. Capillarity is for liquid substances what statics is for solid bodies, although the analogy is somewhat remote, because a real statics of liquids does not exist. In order to explain the cohesion of molecules and the mechanical strength of a

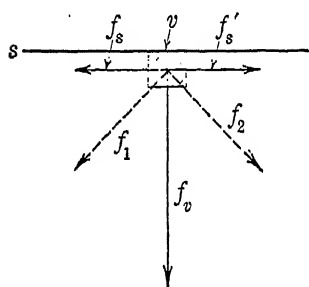


FIG. 1. Forces at the Surface of a Liquid.

solid body the concepts of bending strength, tensile strength, etc., are used. In a liquid, the so-called *surface tension* serves as a measure of the cohesion among individual particles. This tension is a result of the cohesive forces between adjacent molecules. It will now be shown (Fig. 1) how the molecular forces of attraction

give a component in the plane of the free surface of the liquid.

In Fig. 1,  $s$  is the free surface of a liquid and  $v$  is the cross-section of an elementary prismatic volume whose length is perpendicular to the plane of the paper. The surrounding mass of the liquid exerts forces of attraction upon this volume in the direction of the arrow-heads  $f_1$  and  $f_2$ . These forces may be resolved into the vertical component  $f_v$ , and the horizontal components  $f_s$  and  $f'_s$ . The component  $f_v$  is the so-called inner pressure of the liquid, while



the components  $f_s$  and  $f'_s$  generally balance each other and exert no action. It is only when the free surface is in some way artificially distorted out of its symmetry that  $f_s$  may have to be taken into consideration. As an example, Fig. 2 represents a solid body  $b$ , which is partly immersed in a liquid. The component  $f'_s$  evidently disappears, and only  $f_s$  remains, which acts along the whole boundary line between  $b$  and the liquid. It is this latter force that is called the surface tension; it always acts in the plane of the free surface.

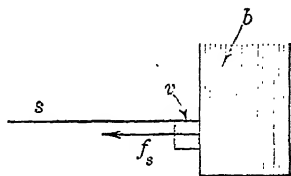


FIG. 2. Surface Tension at the Boundary of an Immersed Body.

Surface tension is defined as the force  $\gamma$  acting upon a boundary surface line 1 cm long, and is usually measured in dynes per

centimeter. The surface tension of liquefied gases is on the average 10, that of organic liquids 30, of aqueous solutions 70, of fused salts 100 to 200, and of molten metals 300 to 1000. Thus it increases with decreasing vapor pressure and is really a measure for the cohesion of a substance.

These facts are of interest from the point of view of electrical insulation, because of the peculiar form of electrical breakdown in liquids, which may be considered as a disguised gas sparkover that overcomes the cohesion forces of the liquid. Thus it may be expected that the breakdown strength should to some extent increase with the surface tension. For details see under

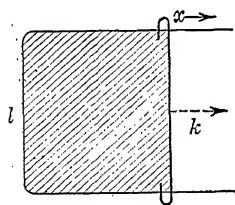


FIG. 3. The Origin of Surface Energy.

*Breakdown*, Section 14.

It is also instructive to introduce the concept of free *surface energy*. Consider a liquid film (Fig. 3) stretched on a frame whose right-hand side may be moved at will, and let an external force  $k$  be applied to this side of the frame; we then have

$$k = 2l\gamma$$

where  $l$  is the length of the movable side of the frame. The factor 2 is necessary because the surface tension  $\gamma$  is acting on both surfaces of the film. If the displacement is  $x$ , then the work done by the force  $k$  is  $2lx\gamma$ . On the other hand, the newly created surface of the film is  $2lx$ . Thus the gain in free energy per unit area is  $\gamma$ . The surface tension  $\gamma$  is therefore also the magnitude of free energy in ergs per unit area, and is called the free surface energy. In many investigations it is preferable to work with the concept of surface energy rather than with that of surface tension.

Surface tension manifests itself wherever a liquid has a free surface, and it is therefore of importance to the applied scientist in a great variety of cases. The free surface always assumes such a shape that all the existing forces are in equilibrium. These forces consist of the surface tension, the force of gravity, and sometimes electrical forces. Here it is advisable to introduce energies instead of forces; use is then made of the familiar law that a system at a given temperature and volume always tends toward a state in which the free energy is a minimum. The free energy consists of the above-mentioned surface energy, the potential energy of the field of gravity, and the electrical energy.

One of the simplest illustrations of this law is that a small free drop of liquid always assumes an approximately spherical shape (for example, a raindrop). The energy due to gravity may be neglected in this case, and the surface energy is obviously proportional to the surface itself. With a given volume a sphere has the smallest possible area.

When small liquid particles are suspended in another liquid and are subjected to an external electrostatic field, they assume a shape different from that of a sphere. When the dielectric constant of the suspended particles is greater than that of the surrounding medium, the electric field attracts the particles, and as a result they become elongated in the direction of the field. This stretching effect continues until the surface tension balances the electric force.

Strictly speaking, it is the tension at the boundary

between the two liquid phases, the so-called interfacial tension, which in this case determines the elongation. Its value is usually lower than that of the free surface tension itself. This question will be further discussed in Section 14, under *Breakdown*.

A further important illustration is the behavior of a liquid in a tube of small diameter and in a narrow gap. In the region of contact a liquid surface is formed which is either concave or convex upward, depending upon the properties of the material of the walls. The causes of these two possibilities will be further discussed below. Here we shall assume the more usual case of a

concave surface of a liquid in a vertical cylindrical tube of radius  $r$  (Fig. 4). As is often the case, the liquid covers the whole inner surface of the tube with a thin film (even above the level of the liquid). This film tends to raise the column of the liquid in the tube, because the free surface, and consequently the surface energy, are thereby reduced. However, the

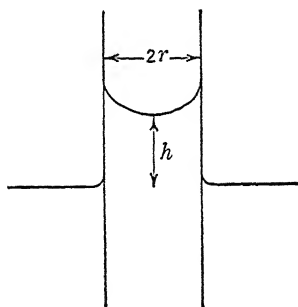


FIG. 4. Rise of a Liquid in a Capillary Tube.

increase in the potential energy due to gravity must also be considered. Let the surface energy be called  $S\gamma$ , where  $S$  is the free surface. The potential due to gravity is  $V\rho gh_m$ , where  $V$  is the volume of the liquid column raised to the average height  $h_m$ ,  $\rho$  the density, and  $g$  the acceleration due to gravity. The liquid column becomes longer until the sum

$$S\gamma + V\rho gh_m$$

becomes a minimum. The mathematical condition for the minimum of a function is that its first derivative with respect to the independent variable equals zero. Let the height  $h$  increase by  $dh$ ; then the differential of the first term in the above expression is  $-2\pi r\gamma dh$ , because the area

of a narrow ring whose surface energy disappears is  $2\pi r dh$ . The differential of the second term is  $\pi r^2 \rho g h dh$ , because the volume of the raised liquid cylindrical slice is  $\pi r^2 dh$ , and it has to be raised by an amount  $h$  counting from the external surface of the liquid. Equating the sum of the two differentials to zero, one obtains after simplification

$$2\gamma = \rho g r h$$

from which:

$$h = 2\gamma / (\rho g r) \quad (1)$$

The height of the column increases with increasing surface tension and with decreasing radius of the tube. This formula is used for experimental determinations of  $\gamma$  from  $h$ , according to the so-called capillary rise method.

A similar phenomenon takes place when a porous substance comes in contact with a liquid. The impregnation of the porous substance is due to the capillary forces, and the process is extremely vigorous because the radii  $r$  of the elementary tubes are exceedingly small. This process is of decided importance, for example in the manufacture of oil-impregnated paper insulation for high-voltage cables. We shall have more to say about this subject in Section 15.

In high-tension apparatus filled with oil it has been observed that the oil often creeps up along the metal parts, such as a plate or wire subjected to a voltage. Some rise also takes place without the electrical forces, according to the same process as described above for a tube. The capillary forces and the force of gravity finally reach equilibrium. When an electrical force is added, it becomes cumulative with the action of the capillary forces, and the two must be in equilibrium against the force of gravity; the oil rises therefore still higher. We shall return to this phenomenon in the discussion of motions under the action of a high voltage. (See Section 11.)

We shall now discuss another essential factor which facilitates an understanding of the phenomenon of capillarity. As has been mentioned above, some liquids form

concave surfaces in narrow tubes and at walls; others form convex surfaces. The shape of the free surface depends upon the behavior of the liquid with respect to the solid wall. We must therefore investigate in general what takes place at the boundary of a liquid, a solid wall, and the air. In this manner we obtain the so-called boundary condition which is indispensable in a description of capillary action.

A knowledge of the value of the surface tension  $\gamma$  of a liquid is not sufficient in order to describe a phenomenon near a solid wall. This is clear because in the derivation of the magnitude of  $\gamma$  we took into consideration only the attraction of liquid molecules among themselves, whereas in the vicinity of a wall the mutual attraction between solid and liquid molecules is also a factor. A free liquid surface in contact with air has an energy  $\gamma$  per unit area. On the boundary between a liquid and a solid another term must be added to the energy; this term is positive when the liquid molecules are repelled from the wall (mercury in glass) and is negative when the wall attracts the liquid molecules (water in glass). Let this term be denoted by  $\gamma'$ . Then the boundary surface tension,  $\gamma_s$ , between the solid and the liquid phase is

$$\gamma_s = \gamma + \gamma'$$

Strictly speaking, another term, the surface tension of the solid phase, should be added; this, however, may be omitted for the purpose of the following considerations.

In most practical cases  $\gamma'$  is negative, and its absolute magnitude is greater than that of  $\gamma$ , so that the total tension,  $\gamma_s$ , is negative. This simply means that the process of building a boundary surface furnishes work instead of consuming energy, and therefore the free energy is negative. The stronger the attraction between the liquid and the wall, that is, the stronger the *wetting*, the more negative becomes  $\gamma'$  and consequently  $\gamma_s$ . The factor  $-\gamma'$  is the measure of the wetting of a wall by a liquid; it is often called the *wetting tension*. Its value determines the behavior

of a liquid in a tube or in a vessel because it settles the boundary conditions. More specifically, the wetting tension determines the so-called *boundary angle*,  $\theta$ , which is the angle between the free surface and the wall (Fig. 5).

The surface tension  $\gamma$  and the boundary tension  $\gamma_s$  act upon the free liquid surface at the boundary line  $l$  (per-

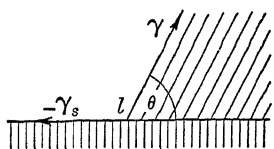


FIG. 5. Boundary Angle.

pendicular to the plane of the sketch). If we assume the position of this boundary line on the wall to be given, the only variable is the slope of the free surface or the angle  $\theta$ . This slope is such that  $\gamma$  and  $\gamma_s$  are in equilibrium. The tension  $\gamma$  acts in the free surface in the direction of the arrow-head; its component in the direction of the wall surface is  $\gamma \cos \theta$  and is directed to the right. It tends to increase the value of  $\theta$ . The boundary tension  $\gamma_s$  acts in the plane of the wall, also to the right; this means that  $-\gamma_s$  (which is generally positive) is directed to the left. This force is due to wetting and tends to reduce  $\theta$ . Consequently,

$$-\gamma_s = \gamma \cos \theta$$

or

$$\cos \theta = -\gamma_s/\gamma$$

so that finally

$$\cos \theta = (-\gamma'/\gamma) - 1 \quad (2)$$

When the wetting is low,  $-\gamma'$  is less than  $\gamma$ , and  $\cos \theta$  is between  $-1$  and  $0$ , so that  $\theta$  is an obtuse angle. With a strong wetting,  $-\gamma'$  is greater than  $\gamma$ ; then  $\cos \theta$  is between  $0$  and  $+1$ , and  $\theta$  is an acute angle. Thus the angle  $\theta$  is determined by the surface tension and the wetting tension; it is often used for the determination of the latter when  $\gamma$  is known.

Our former considerations of the rise of a liquid in a tube, at a wall, or in a porous body may now be consider-

ably enlarged on the basis of the knowledge just obtained. The previously considered instance

$$h = 2\gamma/(\rho gr)$$

was only the most common limiting case, that of a strong wetting. There the angle between the free surface and the wall is 0 (Fig. 4). Our description, according to which a thin film covers the wall and tends to reduce its area, is correct in this limiting case, but not in the general one. When the angle  $\theta$  is finite (for example, acute), one cannot speak of a liquid film any more. The force which causes the liquid to rise is then simply the wetting tension of the wall itself. When the circular boundary line is drawn upward by an amount  $dh$ , a new surface  $2\pi r dh$  of the wall is wetted, so that an amount of energy  $-2\pi r dh \gamma_s$  is lost. Thus, in the foregoing formula (1),  $-\gamma_s$  must be generally used in place of  $\gamma$ . But since  $-\gamma_s = \gamma \cos \theta$ , we have:

$$h = 2\gamma \cos \theta / (\rho gr) \quad (1a)$$

It will be seen from this formula that with a complete wetting ( $\cos \theta = 1$ ) the rise of the liquid column is a maximum, whereas with the smallest possible wetting ( $\cos \theta = -1$ ) a maximum depression must take place in a capillary tube (mercury in glass). On the other hand, the expression

$$h = -2\gamma_s / (\rho gr) \quad (1b)$$

shows distinctly that the wetting  $\gamma'$  and the boundary tension  $\gamma_s$  respectively are the causes which draw the liquid up. Because of the limited validity of equation (2), since  $-1 < \cos \theta < 1$ , it is often advisable in practice to use  $\cos \theta$  in place of  $\gamma'$ , and for  $h$  to use equation (1a) rather than (1b).

The relations just described are of the greatest importance in technical applications. To mention but one of these, in the manufacture of molded artificial insulating materials, such as Bakelite compounds, a liquid mixture is poured into molds, in which it gradually solidifies under

the action of heat and pressure. It is of importance to have a rather low wetting of the form by the mixture, because otherwise the mixture would penetrate into the superficial pores of the mold, and it would be difficult to pry the solidified body loose and preserve a smooth surface. According to equation (1*b*), it is essential in this case to consider simultaneously both the value of the surface tension  $\gamma$  of the mixture and that of the wetting tension  $-\gamma'$ : a greater value of the first and a smaller value of the second are desirable.

It is of interest to note that it is possible to vary  $\gamma$  and  $-\gamma'$  within certain limits, even with a given mixture. Since the variability of  $-\gamma'$  is much greater than that of  $\gamma$ , the former value is the deciding factor. We can go into these relationships only briefly here, because otherwise the discussion would lead us too far. Substances whose solubility in a liquid is low have a tendency to become more concentrated toward the surface layer, as if they tried to get out of the liquid. They are therefore called, with respect to a given liquid surface, active. It can be shown that substances which become more concentrated near the surface reduce the surface tension; this is known as Gibbs's theorem. In this manner the surface tension of almost any liquid becomes reduced by the addition of even a small quantity of some surface-active material.

Since it is impossible to predict in advance how the addition of a substance is going to change the wetting of a given wall surface, it is necessary to resort to experiment. As pointed out by Langmuir, the molecules which reach the surface and become adsorbed there are oriented in some manner. That group of the molecules which has the greatest affinity for the solvent tends to concentrate inward; the other group outward. Thus, the outer layer consists of molecular groups which are the least soluble, and the question is whether these groups have a strong or weak affinity for the material of the wall. This determines whether  $-\gamma'$  is large or small.



The above-mentioned Bakelite mixtures may again be cited as an example. It is often observed that they stick to iron molds and cannot be taken out with a smooth surface. This is probably due to an affinity between phenol molecules and iron atoms. The addition of an organic salt, such as magnesium stearate, helps considerably to remove the molds. The salt molecules are surface-active, and they orient themselves with the stearate group inward and the magnesium ion outward. Magnesium and iron possess a comparatively small mutual affinity, so that  $-\gamma'$  is reduced, and the mixture is not held in the pores of the mold.

*Summary.*—The behavior of a free surface of a liquid is described in terms of the surface tension  $\gamma$ ; the behavior of the boundary between two liquids is described in terms of the boundary tension. The surface tension is a measure for the content of free energy per unit surface. The surface tension determines the form of minute drops in a field due to gravity or to electric charges. In addition, the behavior of a liquid in the vicinity of a solid wall, in a capillary, and in a porous body is affected by the value of the wetting tension ( $-\gamma'$ ), the latter being the amount of work gained in the wetting of a unit surface, owing to the mutual attraction of the two kinds of molecules. The factors  $\gamma$  and  $-\gamma'$  determine the boundary angle  $\theta$ . With perfect wetting, the value of the surface tension  $\gamma$  determines the height of a liquid in a capillary tube or in a porous body. In practice, to prevent adhesion on rough walls, it is advisable to reduce the value of the wetting tension  $-\gamma'$ . This may be accomplished to a considerable degree by the addition of a surface-active substance.

**3. Viscosity.**—If capillarity of liquids be considered analogous to the statics of solid bodies, the phenomenon of viscosity may be compared to the dynamics of solid bodies. At any rate, the phenomena of capillarity and viscosity, from a practical point of view, are two fundamentals in the mechanics of liquids. They are also of the greatest interest to an electrical engineer.

The fundamental molecular process in the preceding section was the molecular attraction. Here we have to consider another elementary process: the collisions which steadily take place between adjacent molecules of a liquid if these molecules are in orderly motion. Part of the kinetic energy of the orderly motion is converted by the collisions into random translation and rotation of molecules, due to heat. The heat content is simply the sum of the energies of such random translations and rotations of the molecules. For a directed motion of the liquid this part of the energy is lost.

Thus during the flow of a liquid, part of the energy of the flow is lost, and the liquid itself becomes warmer. This phenomenon is known as the *inner friction* in a liquid. In hydrodynamics, liquids are described as real or ideal, according to whether they manifest inner friction or not. Ideal liquids are only a fiction introduced in order to facilitate the deduction of hydrodynamic equations.

In nature only real liquids, with inner friction, exist.

It is advisable to define the magnitude of friction by means of a specific number, just as  $\gamma$  designates the magnitude of capillarity. For this purpose consider the motion of a liquid in a pipe in the direction indicated in Fig. 6. The velocity  $u$  of the liquid filaments varies in the transverse direction  $n$ . Consider a plane  $f$  perpendicular to the plane of the paper and assume  $u$  to increase with increasing  $n$ ; then the flow to the right of  $f$  is more intense than to its left. The liquid to the left of  $f$  is accelerated by the portion to the right, which moves more rapidly, and conversely the right-hand part is being retarded by the portion to the left. In other words, a shearing force acts in the plane  $f$ . This force is proportional to the area  $f$ , to the velocity gradient,  $du/dn$ , and to a constant  $\eta$

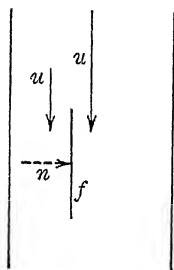


FIG. 6. A Viscous Flow in a Tube.

to the velocity gradient,  $du/dn$ , and to a constant  $\eta$

which characterizes the liquid. Thus the force may be expressed as:

$$\eta f(du/dn)$$

The constant  $\eta$  tells to what extent the more rapidly moving particles are retarded by the slow particles; this phenomenon is brought about by collisions and by a resulting tendency to equipartition of the kinetic energy of the orderly motion. Consequently, the constant  $\eta$  measures the inner friction of the liquid and is therefore called the coefficient of inner friction or the *viscosity coefficient*.

The actual motion of a liquid in a tube or through a porous system is determined by the constant  $\eta$ . We shall consider an important case, that of motion of a liquid in a tube of small diameter. Such motion is of primary importance in the measurement of the coefficient of viscosity. Furthermore, such a flow often occurs in technical applications, particularly with insulating oils: it is this kind of flow that determines the velocity of impregnation of a porous substance and the motion of the oil in a cable.

First of all, let us clearly understand the unit and numerical values of viscosity. The unit of  $\eta$  is 1 poise (named after the investigator Poiseuille). It is the viscosity of a liquid (Fig. 6) which exerts a force of 1 dyne upon 1 sq cm of the surface  $f$  when the velocity gradient in the direction  $n$  is equal to 1 cm/sec/cm. One one-hundredth part of this unit is the centipoise. The viscosity of light liquids is of the order of magnitude of 1 centipoise. For transformer oils,  $\eta$  is about 1 poise, and for glycerin and castor oil 10 poises; for heavier oils it is still higher. The higher the viscosity the lower is the velocity of flow in a tube, and the less the flow is accompanied by eddies; it is to such kinds of flow that the law which we are about to deduce is most applicable.

Fig. 7 represents a cross-section of a cylindrical pipe of radius  $R$ . Let the length of the pipe be  $l$ , and let a liquid

flow in the direction perpendicular to the plane of the paper under the action of a difference of pressure  $p$  applied at the two ends of the pipe. The distribution of velocities of the liquid is the same in any cross-section, but the velocity varies from point to point within the cross-section. However, the space being symmetrical with respect to the axis of the pipe, the velocity  $u$  is only a function of the distance  $r$  from the center. Thus every elementary hollow cylinder

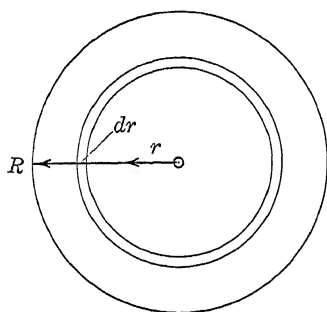


FIG. 7. Flow of a Liquid in a Tube.

of liquid of radius  $r$  and thickness  $dr$  possesses its own velocity  $u$ . Such a flow is called lamellar. Our problem is to determine  $u$  as a function of  $r$ , from the differential equation of the phenomenon. The sum of the forces acting upon an elementary cylinder is equal to zero because the cylinder moves with a constant velocity. The acting forces are

those of pressure and of friction. The total pressure equals  $2\pi r p dr$  (the area of each stub-end times the unit pressure). The total force of friction on the outer surface of the elementary cylinder is  $2\pi r l \eta (du/dr)$ , (lateral surface times the viscosity coefficient times the velocity gradient). On the inner surface of the cylinder the corresponding force of friction acts in the opposite direction, so that the resultant total force of friction is as follows:

$$2\pi l \eta [d(r du/dr)/dr] dr = 2\pi l \eta r [(d^2 u/dr^2) + (1/r)(du/dr)] dr$$

Thus the differential equation is:

$$(d^2 u/dr^2) + (1/r)(du/dr) - p/(l\eta) = 0$$

To solve this equation completely, one has to know the boundary conditions. One of the conditions is:

$$(du/dr)_{r=0} = 0$$

because otherwise there would be a discontinuity in the gradient along the axis of the pipe. The other condition is:

$$u_{r=R} = 0$$

because experience shows that a liquid adheres to a wall. The velocity of the outermost cylinder is zero, and the velocity increases toward the center, being at a maximum along the axis of the pipe. The solution of the differential equation is:

$$u = [p/(4l\eta)] (R^2 - r^2)$$

as may easily be proved by direct substitution.

The total amount  $v$  of liquid passing through a cross-section per second is obtained by integrating  $u$  over all the elementary cylinders; we thus obtain:

$$v = \int_0^R [2\pi r dr p/(4l\eta)] (R^2 - r^2)$$

In this expression the cross-section  $2\pi r dr$  of each cylinder is multiplied by the corresponding velocity  $u$ . After integration we obtain:

$$v = \pi p R^4 / (8l\eta) \quad (3)$$

which is known as Poiseuille's equation. It is of interest to note that the total rate of flow,  $v$ , increases as the fourth power of the radius of the pipe, indicating that the resistance to flow increases very rapidly with a decrease in the diameter of a tube.

The viscosity of a liquid may be determined on the basis of the foregoing principles, using an Ostwald viscosimeter (shown in Fig. 8). The liquid under test is allowed to flow from the spherical vessel shown at the left into the one to the right, and the total time of flow is determined with a stop-watch. The time of flow is proportional to the coefficient of viscosity. The device may be calibrated with

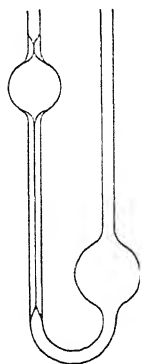


FIG. 8. Ostwald's Viscosimeter.

water, for which  $\eta$  is equal to 0.010 poise at 20° C; absolute values of  $\eta$  may then be determined for any other liquid.

There are other types of viscosimeters better adapted for practical purposes, particularly for oil. Such a viscosimeter is usually a vessel of definite dimensions with an opening in the bottom. The time of emptying such a vessel, multiplied by a factor, gives the viscosity in empirical units. In America, Saybolt's viscosimeter is used, and the unit is called the Saybolt-second. In Germany, Engler's viscosimeter is more common, and the corresponding unit is called the Engler unit. Saybolt-seconds may be converted into Engler degrees by multiplying by a factor which decreases from 0.035 to 0.027 for Saybolt-seconds 30 to 200, and from there on remains constant. A coefficient of viscosity obtained in practical units may be converted into poises; for example, for the Engler degrees (E) greater than 5

$$\eta = [4.07E - (3.52/E)]/(100/\rho)$$

where  $\rho$  is the specific weight of the oil under test.

For very viscous oil, such as is used for an impregnating compound, these devices are not suitable, because the time of outflow becomes too great. For such purposes a falling-sphere viscosimeter may be used. According to Stokes's law (and neglecting the density of the medium), the velocity of fall of a sphere of weight  $P$  and radius  $r$  in a viscous medium of coefficient  $\eta$  is

$$u = (P/6\pi r\eta)$$

The coefficient  $\eta$  may be computed from this formula.

The author has developed a simple device, suitable for comparative measurements, which is shown in Fig. 9. A vessel with double walls contains the oil under test on the inside and water of a definite temperature in the jacket. The bottom of the vessel is provided with an opening into which a cylinder fits so that a thick oil just barely drips

through. The interval of time within which the cylinder falls by a certain number of divisions is then measured. The instrument is calibrated by means of an oil of known viscosity; for other oils the intervals of time of the fall of the cylinder are proportional to the values of the coefficient of viscosity. Of course, the temperature of the oil must always be measured.

For accurate measurements on heavy oils the author has constructed the apparatus shown in Fig. 9a. The

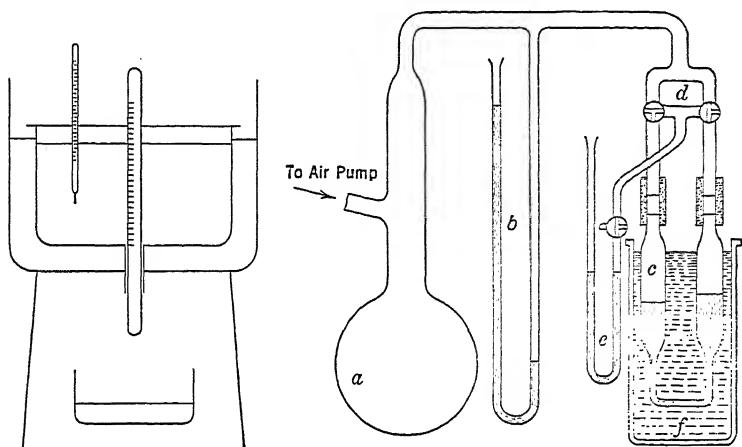


FIG. 9. Gemant's Viscosimeter for Heavy Oils.

FIG. 9a. Another Viscosimeter (by Gemant) for Heavy Oils.

method is based on the capillary principle and makes it possible to study very viscous oils, the sample in the vessel *c* being forced by an excess pressure through a capillary connection at the bottom. This over-pressure is produced in the chamber *a* by a hand pump and is measured on the gauge *b*. Very small changes in the oil level in *c* are indicated in the U-shaped tube *e*, filled with thin oil. With the positions of the three-way stopcocks *d* shown in the sketch, the oil flows from the right to the left compartment of *c*. A constant temperature is maintained by means of the bath *f*. The vessel *c* is interchangeable with others which have

capillary connections of different diameters, so that light as well as heavy oils may be studied. The device is best calibrated with castor oil.

A few words should be said about the dependence of viscosity upon temperature. Variations with temperature are so great that any measurements of viscosity are of value only if the temperature has been accurately considered. The coefficient of viscosity decreases to a considerable degree with increasing temperature. The reason for this decrease lies in higher molecular velocities. The forces of attraction between molecules are thereby overcome, and the number of collisions decreases, so that a smaller percentage of the orderly velocity is lost in friction. When the liquid is cooled molecular velocities become smaller, and the molecules are more steadily attracted by their neighbors; the number of collisions increases, and the kinetic energy

is converted to a greater extent into heat energy.

This relationship between viscosity and temperature is a logarithmic one; that is,

$$\log \eta = \log \eta_0 - \alpha t$$

where  $\eta_0$  and  $\alpha$  are constants. Strictly speaking, the formula is of the form

$$\log \eta = \log \eta_0 + (\alpha'/T) \quad (4)$$

where  $T$  is the absolute temperature. For small intervals of temperature the first formula holds approximately true.

It is always instructive to obtain a curve of  $\eta$  as a function of  $t$  for a given dielectric. Such a curve for transformer oil is shown in Fig. 10; the abscissas are values of  $1/T$  corresponding to the range between  $-10^\circ$  and

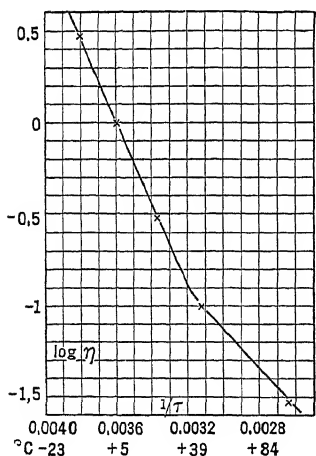


FIG. 10. Variations in Viscosity of a Transformer Oil with Temperature.



+100° C. The ordinates are the common logarithms of viscosity in poises, corresponding to values of viscosity of 3.0 to 0.03. The relationship is approximately a straight line, bent only at 0.00324, corresponding to 35° C and 0.17 poise. Below 35° C the slope is 2.2 times greater than above this limit. Above 35° C we have a pure liquid state, whereas under 35° there is a certain "stickiness," indicating a definite change in the structure of the oil. Below -30° C there is again another bend in the curve, because the oil begins to solidify. Thus a discontinuity in the slope of a viscosity curve as a function of temperature indicates a definite change in the structure of the liquid. See Section 17 for the hysteresis phenomenon in the viscosity curve.

Glass in its viscous liquid state behaves similarly. The curve of  $\eta$  as a function of  $t$  usually has two bends. One lies at about 400° C, and corresponds to the so-called transformation point of glass, similar to solidification of an oil. The second point lies at about 800° C and is known as the aggregation point. This is a change from the viscous to a thin liquid state, corresponding to oil at about 35° C. In the thin fluid state the molecules are all separate, whereas in the viscous range they are grouped together, forming rather large aggregates. The curve of variation of viscosity with the temperature is usually less steep within the liquid and the solid range; it is more steep in the viscous range, indicating greater variation with the temperature.

The viscosity of oils and of impregnating compounds, and its dependence upon the temperature, play extremely important parts in high-voltage cables; in Section 15, dealing with these, we shall return to the results of this section.

In conclusion we shall discuss briefly the plasticity of some viscous fluids. According to Poiseuille's equation, (3), the rate of flow  $v$  through a tube is proportional to the difference in pressure  $p$ ; that is,

$$p = kv$$

where  $k$  under otherwise equal conditions is a measure for the inner friction. An experimentally determined straight-line relationship between  $p$  and  $v$  should evidently pass through the origin. There are cases (Fig. 11), however, where the straight line intersects the axis of ordinates at a positive value  $p_0$ , so that the above equation becomes

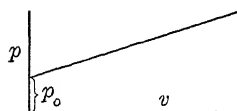


FIG. 11. Flow Curve of a Plastic Body.

$$p = p_0 + kv \quad (5)$$

This indicates that the liquid possesses a certain amount of plasticity. Up to a certain driving pressure,  $p_0$ , there is no motion of the liquid, just because it is plastic. The factor  $p_0$  may be called the plasticity constant. When the pressure exceeds  $p_0$ , the original equation holds true for  $p - p_0$ .

Probably the reason for this phenomenon is that a liquid possesses a certain amount of structure which is destroyed only at a pressure  $p_0$ , and then a flow becomes possible; hence, another name for plasticity is structural viscosity. Such a

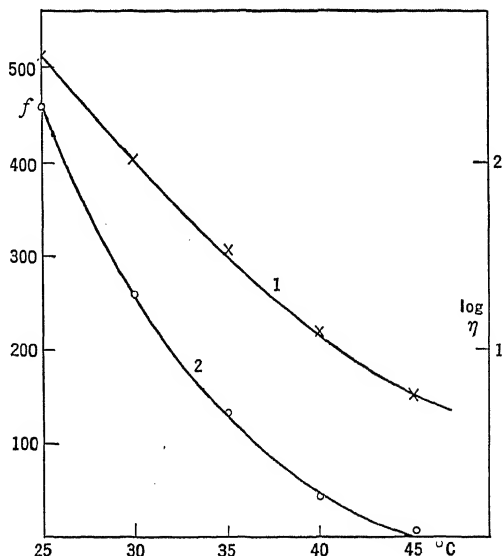


FIG. 11a. Viscosity (1) and Flow-rigidity (2) of Shell Co.'s Cylinder Oil B 13.

structure may be due to colloidal particles which possess a certain amount of inner cohesion. The phenomenon has been investigated by a group of scientists led by Freundlich, and also by E. Hatschek.

By means of the apparatus shown in Fig. 9a, the author has demonstrated that there are oils which possess plasticity. The results of measurements on some Shell cylinder oil B13, furnished by the Rhenania-Ossag Co. of Hamburg, are shown in Fig. 11a. Curve 1 gives logarithms of the values of viscosity, and curve 2 the so-called flow-rigidity coefficient  $f$ ; using the plasticity constant  $p_0$  (defined in equation (5)), the expression for  $f$  is

$$f = 3rp_0/(8l)$$

where  $r$  is the radius of the capillary and  $l$  its length. It will be seen that plasticity appears at  $45^\circ$  C and rapidly increases with falling temperature.

It is worth noting that there seems to be no connection between the factors  $\eta$  and  $f$ . For example, for oil B13, plasticity becomes noticeable at a viscosity of 10 poise, whereas for Shell cylinder oil B4a there is no trace of plasticity at  $5^\circ$  C corresponding to a viscosity of 1600 poise.

It may be mentioned that the theory here given concerning plasticity plays only the rôle of a simple working hypothesis. Especially equation (5) and the plasticity constant  $f$  are only empirical. Several authors (W. Herschel, Hencky, etc.) have called attention to the fact that in this equation there must be quadratic terms also. Recently Weissenberg has formulated a new theory of elasticity which leads to the following equation of flow:

$$u = K(p/\eta) \cosh (p/\gamma)$$

in which  $K$  is a geometrical constant and  $\gamma$  an elastic constant. As one may see by expanding the hyperbolic function in this equation, there is no constant term at all. The above-mentioned experiments of the author on heavy oils, extended over a wider range of initial conditions, show that the rate of flow increases more rapidly than according to a straight line.

*Summary.*—In any orderly flow of a liquid there are collisions of adjacent molecules, with the result that part

of the directed velocity is lost and converted into random heat motion. This phenomenon is called inner friction, and its intensity is measured by a number known as the coefficient of viscosity  $\eta$ . Viscosity is of paramount importance in all phenomena of liquid flow. For flow in tubes of small diameter (the so-called lamellar flow) Poiseuille's equation deduced above holds true. Most of the measurements of viscosity briefly sketched above are based on this equation. The viscosity of a liquid decreases very rapidly with increasing temperature, according to a logarithmic law. The curve which shows this relationship has discontinuities of slope at places at which the inner structure of the liquid is changed.

Some liquids of colloidal nature manifest so-called plasticity, due to an inner structure. A viscous flow begins only after the applied pressure has exceeded a certain minimum value  $p_0$ .

**4. Conduction of Heat.**—Of the whole field of the physics of heat the subject of heat conduction is of particular interest to the electrical engineer. However, since the conditions involved are practically identical for solids and for liquids, we shall treat them here only briefly. The topic could not be omitted altogether without leaving our discussion incomplete.

According to an empirical law of Wiedemann and Franz, there is a certain parallelism between electric conductivity and heat conductivity.\* Accordingly the dielectrics, and particularly the oils, are rather poor conductors of heat, whereas metals and damp bodies are good conductors.

We shall begin with the differential equation of the flow of heat. Let the rate of the flow of heat in a certain chosen direction  $n$  be  $j$ , in calories per second per square centimeter. Then we have

$$j = -\lambda(\partial T/\partial n) \quad (6)$$

\* Strictly speaking, this law is valid only for metals; however, in a certain sense it may be extended to apply to other substances.

where  $T$  is the temperature and  $\lambda$  a constant known as heat conductivity. Since the unit for  $j$  is  $1 \text{ cal}/(\text{cm}^2 \text{ sec})$ , the unit for  $\lambda$  is  $1 \text{ cal}/(\text{cm sec deg})$ . The reciprocal of  $\lambda$  is usually called heat resistivity, and in the absolute units is measured in  $\text{cm sec deg/cal}$ . In place of the calorie the watt-second may be introduced; the heat resistivity is then measured in  $(\text{cm deg})/\text{watt}$ . For conversion use the formula

$$1 \text{ watt-sec} = 0.239 \text{ gram-cal}$$

The following numerical values will give an idea of the order of magnitude of the coefficient  $\lambda$ , in  $\text{cal}/(\text{cm sec deg})$ . For water,  $\lambda$  is 0.0013; for benzene, paraffin, and cylinder oil, 0.0003; for paper, about the same value; for ordinary soil, 0.005. Metals are the best conductors of heat; thus for copper  $\lambda$  is about 0.9.

Using equation (6), it is possible to determine the temperature distribution within a given system in a steady state. An analogy will sufficiently explain the method. In the theory of static electricity the following familiar equation is used

$$D = - \epsilon(dU/dn)$$

where  $D$  is a dielectric displacement,  $\epsilon$  is the dielectric constant, and  $U$  the electric potential at a point. This equation is completely analogous to equation (6);  $\lambda$  and  $\epsilon$  are both material constants,  $j$  and  $D$  are vectors which satisfy the properties of a source field. Heat sources correspond to electrical charges; in regions in which there are no sources the total flux of heat or of electrical displacement remains constant in all cross-sections of a tube of flux, and also at the boundary surfaces between two different media. There is therefore a complete formal analogy between  $j$  and  $D$ . Therefore  $T$  and  $U$  must also be analogous quantities, and the temperature may be thought of as a kind of potential to which the heat energy is raised at different points.

In practice it is of importance to know the temperature

distribution. From the preceding considerations it follows that this problem may be solved exactly like the problem of potential distribution, which is well known in the theory of electricity. For example, if a heat conductor is a slab, the temperature distribution normal to the end planes is always linear. If there are several thin layers in series, with materials of different heat conductivity, the value of the temperature gradient in each is inversely proportional to the corresponding value of  $\lambda$ .

Of particular importance are the cases in which heat is carried away through oil, for example, in transformers and in power cables with insulation consisting of impregnated paper. The source of heat is usually cylindrical, whether it be the core of a transformer or the copper conductor in a cable. In both cases the oil is also constrained by containers of cylindrical shape. Of course the ambient medium has not the shape of a cylinder, but in the first approximation it also may be considered cylindrical, for example, for a cable laid underground.

In all such cases the temperature is a logarithmic function of the radius (Fig. 12), as is the electrostatic potential with a cylindrical distribution of charges. For example, let  $R$  be the radius of a cross-section of an oil container and  $R_0$  the radius of that surface of the surrounding heat conductor at which the temperature may be kept constant at a value  $T_0$ . Let the heat conductivity of oil be  $\lambda$  and that of the surrounding medium  $\lambda_0$ . Then for any point inside the oil, at a distance  $r$  from the center and at a temperature  $T$ , we have

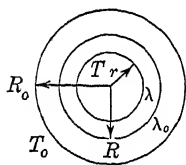


FIG. 12. Conduction of Heat with Axial Symmetry.

$$T - T_0 = (J/2\pi) \left[ (1/\lambda_0) \ln(R_0/R) + (1/\lambda) \ln(R/r) \right] \quad (7)$$

where  $J$  is the total steady heat current per unit length of the cylinder, and the symbol  $\ln$  stands for "natural logarithm." In an electric cable let the radius of the

conductor be  $r_0$ , the electric current  $I$ , and the electric resistivity of the material of the conductor  $\rho$ ; then

$$J = I^2 \rho / (r_0^2 \pi)$$

In this manner the temperature distribution in a dielectric may be determined (at least in simple cases) when the dimensions of the conductors and the magnitudes of the currents therein are given. In practice  $r_0$  is sometimes given, and the highest permissible temperature rise at the surface of the inner conductor is prescribed (for example,  $50^\circ \text{C}$ ). Then from the foregoing equation the permissible current  $I$  may be readily computed as a function of  $r_0$ ;  $T_0$  is simply the known ambient temperature.

The next step is to solve the problem of heat conduction when the heat flow is not steady, that is, for transient phenomena such as switching in or out. The heat current  $j$  is no longer constant in all cross-sections of flow, because in a non-stationary state, heat may accumulate in certain regions. In other words,  $j$  may have a derivative  $\partial j / \partial n$ , so that equation (6) gives

$$\partial j / \partial n = -\lambda (\partial^2 T / \partial n^2)$$

The derivative  $\partial j / \partial n$  is the amount of heat flowing out of a cubic centimeter of material per unit time, because the total heat current is greater by this amount at the point of exit than at the point of entrance. Hence the temperature of that particular unit volume must decrease. Let the density of the material be  $d$  and its specific heat  $c$ ; we then have

$$\partial j / \partial n = -cd(\partial T / \partial t)$$

where  $t$  is time. Equating the right-hand sides of the foregoing equations, we finally obtain:

$$\partial T / \partial t = (\lambda / cd)(\partial^2 T / \partial n^2) \quad (8)$$

Of course this equation is not valid except when a flow of heat takes place in one direction only, that of  $n$ ; in a more

general case the equation must be generalized accordingly. At any rate, it is the fundamental differential equation in partial derivatives for problems of non-stationary conduction of heat; its integration gives an answer in various specific cases. The factor  $\lambda/cd$  is sometimes called the thermometric conductivity, or diffusivity, and is denoted by  $a^2$ . This factor indicates how rapidly the temperature at a given point may change with a given temperature distribution in space. The change is the more rapid the greater the conductivity  $\lambda$  and the smaller the specific heat  $c$ , because in this case a smaller amount of heat energy is sufficient to bring about a desired temperature change. For example,  $a^2$  for petroleum is equal to  $0.0008 \text{ cm}^2/\text{sec}$ .

The solution of equation (7) in a given case is rather involved and usually is possible only in terms of infinite series, which, however, converge rather rapidly. We shall not go into a mathematical representation of these series, and shall only make the following remarks. As a first very rough approximation a series may be replaced by its first term; for a cooling body the following expression is obtained for the excess temperature at any point over  $T_0$ , that of the surrounding medium:

$$T - T_0 = f(n)e^{-t/\tau}$$

In this expression  $f(n)$  is the temperature distribution at the time  $t = 0$ , which may be determined from the given initial conditions. The temperature decreases exponentially with the time.  $\tau$  is the so-called time constant; the greater it is, the more slowly the temperature equalization takes place. For a body whose temperature increases we have the equation

$$T - T_0 = \phi(n)(1 - e^{-t/\tau})$$

where  $\phi(n)$  denotes the temperature distribution in the final steady state.



The order of magnitude of the time constant is roughly given by the approximate formula

$$\tau \sim l^2/a^2 *$$

In this expression  $l$  is of the order of magnitude of the thickness of the heat conductor (in a cable, that of the thickness of the insulation), and  $a^2$  is the diffusivity of the particular substance. Introducing for  $a^2$  its value,  $\lambda/(cd)$ , the foregoing equation becomes:

$$\tau \sim [c(ld)/(\lambda/l)]$$

It will be seen at once that this is the reciprocal of the diffusivity of the whole thickness of the body. Thus the greater the heat conduction of the whole body and the smaller its total heat capacity, the more rapidly heat equalization takes place.

*Summary.*—The relationships in heat conduction are briefly discussed. Of importance for a liquid dielectric is its heat conductivity  $\lambda$ . In a steady state the temperature distribution is analogous to that of an electrostatic potential. Non-stationary heat-flow phenomena are determined by the diffusivity, or thermometric conductivity,  $a^2$ . As a rough approximation, the temperature may be assumed to vary with the time as an exponential function whose time constant is determined by the reciprocal value of the diffusivity.

\* The symbol  $\sim$  means "approximately equal."

## CHAPTER III

### PHYSICO-CHEMICAL BEHAVIOR

5. **Solubility and Gas Absorption.**—Among the various phenomena of liquids in the domain of physical chemistry one of the most important from the point of view of dielectrics is the equilibrium between a liquid and other substances. Impurities are unfavorable in various respects, and therefore it is an undesirable property of a liquid dielectric to admit them, whatever their degree. For this reason some essential points in the theory of solution will be explained below.

The relations may be best understood by starting with the so-called phase rule given by Gibbs. To this end the concepts of phase, component, and degree of freedom must first be explained.

By a phase is understood a *physically* homogeneous part of a closed system. For example, a liquid in contact with a solid body is a system with two phases; a liquid with a gas above is also a two-phase system.

On the other hand, components are the *chemically* homogeneous parts of a closed system. Thus transformer oil and water are two components, irrespective of whether the water is in the liquid form, in the form of vapor, or even dissolved in oil.

By degrees of freedom are meant those conditions of a system which may be chosen entirely at will. Among such conditions may be mentioned in particular the temperature, the pressure, and the concentration of a dissolved substance. For example, transformer oil alone has two degrees of freedom—its temperature and the pressure to

which it is subjected. Both conditions may be chosen at will.

Let the number of phases of a system be  $\beta$ , the number of its components  $\alpha$ , and the number of degrees of freedom  $F$ . Then, according to Gibbs's rule,

$$F = \alpha - \beta + 2 \quad (9)$$

with the added condition that  $F \geq 0$ . For any given system  $\alpha$  is immediately known;  $\beta$  may vary with the conditions but may also be assumed to be known. Equation (9) gives the number of independent variables, or degrees of freedom.

For a better understanding of this rule let us consider benzene as an example. Liquid benzene alone forms a system with  $\alpha = 1$  and  $\beta = 1$ . Consequently  $F = 2$ , the temperature and the pressure being arbitrary. Liquid benzene and its vapor together constitute one component with two phases; hence  $F = 1$ . The temperature may be chosen at will, but the vapor pressure becomes determined thereby. If solid benzene is also present, then  $\alpha = 1$  and  $\beta = 3$ ; consequently  $F = 0$ . This means that the three phases may coexist in an equilibrium only at a definite temperature and a definite pressure; we then have the so-called triple point.

Let us now see what consequences may be drawn from Gibbs's phase rule for our particular problem. Let a liquid dielectric, say an oil, its vapor phase, and a solid body be given, the latter being in contact with the oil. There are two components and three phases; consequently  $F = 1$ . In practice the adjustable variable is the temperature, which determines the rest. The temperature determines the vapor pressure and also the concentration of the solid substance in the oil. Hence, the concentration is uniquely determined by the temperature. The essential point of this conclusion is that there always must be some solubility of a solid in the liquid phase. We often speak loosely of insoluble substances, but this is not correct.

The solubility may be very small, but it is always finite and a function of the temperature. In this sense, even metals possess a certain solubility in liquids. This statement may also be proved in another strictly thermodynamic form, but it really follows from the phase rule, equation (9).

This solubility should not be confused with chemical phenomena, for example, with the dissolving of a metal in an acid, whereby the metal is chemically converted into a salt. Physical solubility leaves the molecules entirely unchanged, any possible change being of a secondary nature. The concentration  $c$ , which is established at the contact of a solid body with a liquid phase, always refers to unchanged molecules.

Such minute solubilities as those mentioned above are generally inconsequential for the dielectric properties of a liquid, unless the solubility is of sufficient magnitude to be detectable by chemical means. For dielectric purposes such solubilities as the last should be avoided as far as possible. For example, solid inorganic salts are practically insoluble in liquid dielectrics, but water as a second phase is always dangerous. The above considerations are also applicable when a second liquid phase, such as water, instead of a solid phase, is in contact with a dielectric. The solubility of the water may always be determined chemically.

Generally speaking, the solubility of a solid or liquid substance in a principal liquid component increases with the temperature. There are a few exceptions to this rule, but generally substances behave in this manner. Thus when water is in contact with oil, and the temperature of the system is raised, more and more water will go over into the oil phase. This behavior must always be kept in mind when one is trying to maintain the quality of an oil.

The relations are different when the second component is not a solid or a liquid, but a gas. We then have again two components, but only two phases, so that in accordance

with equation (9) there are two degrees of freedom. They are the temperature and the pressure, and both may be varied at will. Thus the concentration of a gas in an oil is a function of two independent variables.

For variations of solubility with pressure, Henry's distribution law holds true as a first approximation; according to this law the ratio of the concentrations of a substance in two phases is constant at a constant temperature. The higher the pressure the greater the concentration of gas in the oil, that is, the amount of gas per liter of oil. However, if one considers not the weight of the dissolved gas, but the volume absorbed at a given pressure, it will be seen that this volume must remain constant, because according to the fundamental law of gases the density of a gas increases directly as its pressure. The absorption coefficient is defined as the volume of a gas absorbed by a unit volume of a liquid at a given temperature. The coefficient so defined is independent of the pressure, because although the quantity of the dissolved gas increases as the pressure, the amount contained in a given volume of gas increases in the same proportion.

The foregoing relationship holds true only at a constant temperature. At a constant pressure and variable temperature the absorption coefficient also varies. The absorption coefficient should preferably be referred to the gas volume at  $0^{\circ}\text{C}$ , in order to make it independent of the expansion of a gas with the temperature. Now the factor  $a$  determined in this manner decreases with increasing temperature. Thus the behavior of a gas is opposite to that of a solid or a liquid. With decreasing temperature the tendency of a liquid to dissolve gases or vapors increases, because at a lower temperature the motions of gas molecules due to heat are more readily overcome by the forces of attraction in the liquid.

The reason that adjacent solid and liquid phases behave in a manner opposite to that of gases is that their vapor pressure increases considerably with rising temperature.

Therefore, the pure temperature effect is masked by the action of a rapidly increasing pressure. This causes an increase in the solubility with increasing temperature. When there is only a gas phase above a liquid, the pressure may be kept constant, and the pure temperature effect is manifested to its full extent.

The solubility of gases in liquids varies considerably, depending upon the nature of the components. Water absorbs large quantities of gases. The coefficient  $a$  is smaller for oil; thus  $a$  varies from 0.2 to 0.1 for oxygen and nitrogen. Carbon dioxide is absorbed much more ( $a = 1.2$ ); the absorption of the inert gases, such as neon and helium, is much less ( $a = 0.05$  to  $0.02$ ). Between  $20^{\circ}$  and  $70^{\circ}$  C the variation with the temperature is not very great, and the decrease in the value of the absorption coefficient is about 5% for every  $10^{\circ}$  C.

Dissolved gases are harmful in liquid dielectrics; the reason for this is explained in Section 13. The laws for  $a$  discussed above may be used for the removal of gases, as will be explained below. Of all other dissolved substances water in particular must be guarded against. Usually it is not water in its liquid state but its vapor that is in contact with oil. Therefore the methods used for removal of gases are applicable also to water.

The discussion so far has been limited to an established equilibrium between a liquid dielectric and admixtures. The second question is how fast such an equilibrium is established, that is, what is the velocity of a process of solution and absorption. The following facts should be kept in mind: the layers of a liquid in immediate contact with a gas phase may be considered as being always in equilibrium with the gas. Therefore the velocity in question depends upon the progress of the phenomenon within the liquid itself. This is an ordinary diffusion process, in which the following factors should be considered:

(a) The mobility of gas molecules; this is a quantity which may also be computed theoretically. The smaller

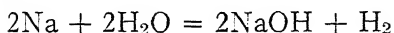
the gas molecules, the less viscous the liquid dielectric, and the higher the temperature, the greater is the mobility.

(b) The geometric form of the container; the greater the horizontal cross-section and the smaller the depth of the liquid, the more rapidly an equilibrium is established. This is a factor common to all flow phenomena. If the cross-section of the oil is widely different at various depths, the resistance to diffusion is mainly determined by the narrowest place. This is true for all kinds of resistances in series.

(c) Whether the liquid is at rest or moving is also of importance for the value of the velocity of absorption. With any motion of the liquid the gases are carried from place to place by convection, the concentration gradient at the surface increases considerably, and the diffusion is thereby facilitated. Thus the velocity of absorption is greatly increased by any motion of the liquid.

The physical laws above described find an important application in the de-gassing and drying of dielectric liquids. The method used with high-voltage cables will be described in Section 15. Here we shall describe only laboratory methods.

The removal of water from a volatile substance, such as benzene, is of less interest to a practical engineer; this is a more purely chemical process. The essential method for the removal of water consists in the use of metallic sodium, which is forced into the liquid by a press, in the form of thin thread. The sodium combines with the water, forming sodium hydroxide:



The hydrogen gas escapes. After the shiny metallic thread becomes covered with a gray deposit the sodium is renewed.

Of more importance is the method used for oil. The principle of the removal of water and occluded gases is based primarily upon the variations of the absorption

coefficient  $\alpha$  with temperature and pressure. Since  $\alpha$  decreases with increasing temperature, a high temperature is favorable for purification. Although  $\alpha$  is not a function of the pressure, the weight of the absorbed gas is proportional to the external pressure; consequently a low pressure is used. The temperature must not exceed  $110^{\circ}\text{C}$ , because if it does the oil will begin to become oxidized (see Section 7). In order to have a low gas pressure the space above the oil is evacuated; the higher the vacuum, the more effective the operation. In order to lower the partial pressure of the water vapor, tubes filled with

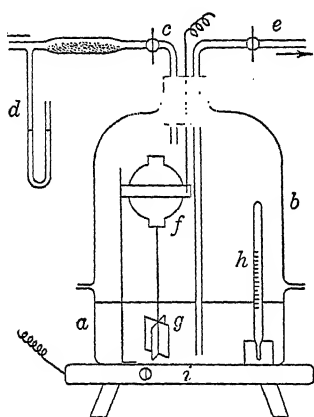


FIG. 13. An Apparatus for Removing Air from Oil.

phosphorus pentoxide are connected between the pump and the oil container. Phosphorus pentoxide absorbs moisture to a high degree and must be renewed from time to time.

In this manner a very favorable absorption equilibrium may be approached. Measures may be taken to increase the speed of the process. The simplest method is to set the oil in motion, for example, with a stirring arrangement operated by a motor.

These principles are embodied in the apparatus shown schematically in Fig. 13. A metal dish  $a$  contains the oil to be purified and is closed air-tight by means of a glass bell  $b$ . The tube  $c$  connects to the pump, through a container with phosphorus pentoxide and a manometer  $d$ ; the tube  $e$  is used for pumping out the purified oil. An electric motor  $f$  is provided with a stirring attachment  $g$ ;  $h$  is a thermometer, and  $i$  a heating plate.

After such a treatment for about twelve hours, in a vacuum of a few millimeters of mercury at  $110^{\circ}\text{C}$ , the drying and purification of oil should be practically complete.



Before closing this section, it is desirable to call attention to a relatively simple experimental method for measuring the absorption coefficient (Fig. 14). The absorption vessel *a*, preferably spherical and of about 200-cc volume, has two outlets with stopcocks *b* and *c*. Initially, *b* is connected with the pipe *e* of Fig. 13, and *c* is connected to a pump; both connections are shown by dotted lines. Completely de-gassed oil is drawn into *a* until the vessel is completely full up to the stopcock. Then *b* is connected with the gas bomb *e* and the pressure gauge *f* by means of a thick-walled rubber hose *d* which must have no gas leaks. The outlet *c* is then disconnected from the pump, the stopcock *b* opened, and while the oil is allowed to flow out at *c* by carefully tipping the vessel, part of the oil is displaced by the gas from *e*. Since the total

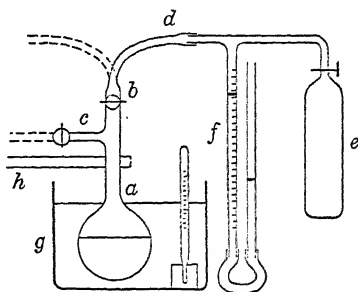


FIG. 14. An Apparatus for Measuring Gas Absorption of Oil.

volume of *a* is known, and that of the oil poured out may be measured, the volume  $v_0$  of the remaining oil becomes known. The flow of gas from *e* is now stopped, and the difference of levels in *f* is accurately read off. Since the barometric pressure is known, so is the gas pressure in *a*. The gas must be admitted quickly, because no appreciable absorption will take place during a short time. The vessel *a* is now placed in the thermostat *g* (with a heating plate and a thermometer) and connected with a shaking device by means of the connecting rod *h*. The stopcock *c* and the hose connection *d* at *b* must be absolutely airtight. When the shaking begins, one may observe the left-hand meniscus in *f* to rise, as a sign that the absorption process has begun. By raising the right-hand branch the original difference of levels may be re-established. This is done until the level in *f* varies no longer. In about an

hour the absorption process is usually finished. Since the left-hand branch is calibrated in cubic centimeters the volume  $v$  of the absorbed gas may be read off directly.

In order to compute  $a$  it is necessary to take the temperature into consideration. If the absolute room temperature is  $T$  (on the Kelvin scale), the absorbed gas at  $0^\circ \text{C}$  will have a volume  $273v/T$ . Consequently

$$a = (273/T)(v/v_0)$$

This method permits the velocity of absorption to be measured also. One has only to read the rise of the left-hand meniscus at exactly equal intervals of time, and this will give directly the time rate of the process.

In Section 15 (high-voltage cables) further details on de-gassing will be given, and some phenomena will be described relative to the velocity of absorption of gases by an oil.

*Summary.*—An equilibrium of solutions is treated on the basis of Gibbs's phase rule for a solid or liquid phase in contact with a liquid dielectric, and for a gas which forms a system with a liquid dielectric. In the first case the amount of solute is a function of the temperature only, whereas in the second it is also a function of the pressure; by suitable definition, the absorption coefficient  $a$  may be made independent of the pressure. In the first case the solubility of the foreign substance in the liquid dielectric increases with increasing temperature; in the second, it decreases with increasing temperature. The time rate of establishing an equilibrium, in other words the velocity of absorption, depends also upon some other determining factors (the form of the container, the motion of the liquid, etc.). Removal of electrically harmful foreign substances, that is, drying and de-gassing of oils, is discussed on the basis of these laws. In conclusion a simple method is described for measuring the absorption coefficient.

**6. Colloidal Structure.**—It has been shown in the preceding section that solid or liquid substances have a defi-

nite solubility in a liquid dielectric, determined by its temperature. Consider a very small quantity of a solid dielectric, such as paraffin, dissolved in a transformer oil by heating the whole system up to about 40° C. By gradually cooling the system a point is suddenly reached at which the solution is exactly saturated. With further cooling, part of the paraffin should become deposited as a solid phase. This does not always take place; the system may continue as a single phase, only it becomes slightly turbid. The paraffin has been actually precipitated, not, however, as a coherent solid phase, but in the form of innumerable small particles which continue to remain suspended in the oil.

When such particles are solid and comparatively large, so that they may be distinguished under a microscope, the system is called a suspension; when the particles themselves are liquid, it is called an emulsion. When the particles are so small that they can be distinguished only with an ultramicroscope, the distribution is called sub-micronic; when the particles cannot be separately recognized at all, the distribution is called amicronic. When the particles are not separate but are connected with each other by means of appendages, so as to form an interconnected network, the system is known as a gel. All such systems are generally called colloidal solutions, which are distinguished from each other by the smallness of dimensions of the second phase ( $10^{-3}$  down to  $10^{-6}$  cm).

That the particles do not precipitate as a solid phase, but remain suspended, is due to several factors. With sufficiently small particles the heat motion is a determining factor, just as gas molecules occupy the whole available space because of the vibrations due to their kinetic energy. In this case the density of particles (the number per unit volume) in different horizontal layers of a sufficiently tall vessel is greater towards the bottom than on top, because of the force of gravity. Such a distribution of density is observed in gases, for instance in the atmosphere,

and it also holds true with colloidal solutions. This property of solutions is made use of in the determination of the magnitude of particles. The degree of non-uniformity of density at different altitudes increases with the diameter of particles, according to a definite law.

With somewhat larger particles the density distribution, computed according to this theory, does not check with the observed distribution, which is much more uniform. Consequently there must be other causes which favor a more uniform distribution of particles. As has been mentioned above, when the limit of solubility has been exceeded, the dissolved portion of the admixture is in the form of separate molecules, whereas the precipitated part is in the form of larger aggregates. The forces which hold the molecules in the solution are also partly active in these larger aggregations. Through their auxiliary valences the particles are bound to the solvent at their mutual boundary surfaces, and thereby prevented from flocculation. This phenomenon is known as solvation of colloidal particles.

A second stabilizing factor is the existence of certain electric charges on the particles. Such particles are often (although not always) surrounded by a so-called electric double-layer. Surface-active substances which are accumulated near the boundary surfaces and are adsorbed to them were mentioned in Section 2. It often occurs in liquids that with two kinds of dissolved ions of opposite sign one kind is much more strongly adsorbable than the other. Consequently, electric charges of one kind will be predominant at the boundary, and the surface will become charged accordingly. Ions of the opposite sign form a so-called cloud about such charged particles. This is sometimes expressed by saying that the inner layer of a double-layer more closely resembles a film, and is monomolecular, whereas the outer layer consists of more diffusely distributed charges. When two particles approach each other, their attractive forces would cause them to unite into one particle, but their electric charges repel each

other and prevent the union, so that the particles again separate. While such double-layers are undoubtedly a factor in dielectrics rich in ions, it is a question to what extent they exist in highly insulating oils.

Among many remarkable properties of colloidal systems is the above-mentioned opalescence, caused by partial absorption of transmitted light by the particles. In oils, blue and green radiation is often observed in the reflected light. Although this may be a purely molecular phenomenon, the so-called fluorescence, yet it may also often be a Tyndall effect due to scattering of light by the small particles. A Tyndall beam of light differs from a fluorescent beam in being polarized. The intensity of Tyndall light in some cases is proportional to  $\mu r^3 \nu^4$ , where  $\mu$  is the quantity of matter in the dispersing phase per unit volume,  $r$  is the radius of a particle, and  $\nu$  the frequency of the scattered light. However, the exponent of  $r$  depends upon the nature of the particles. Thus, the intensity of Tyndall light may be used as a basis for the determination of the magnitude of particles. Such dispersion of light is much more pronounced in a heavy oil than in a thin one, because heavy oils contain more colloidal admixtures.

Some deposits in an oil may also be recognized with a polarization microscope. The light transmitted through a sample is previously polarized by a nicol prism; a second nicol, the analyzer, is placed over the eyepiece and turned  $90^\circ$  with respect to the first one. The field of vision is then dark, and only the deposits appear as bright specks. Fig. 15 is a photomicrograph of a cylinder oil, and Fig. 15a is one of an oil containing resin. Because of being charged by the acid contained in the resin, the particles seem to be still more dispersed. This method also shows that heavy oils contain more suspended matter than thin ones.

The reason for this is as follows. The lower the viscosity of an oil, the smaller are the molecular chains which it contains, as small molecules have a comparatively lower mutual friction. Thus a light transformer oil contains

many components with relatively small molecules, which are considerably above the point of solidification. On the other hand, a highly viscous oil contains components which are just above the point of solidification at room temperature, while some especially long molecular chains are already solid even at room temperature and therefore are precipitated as a dispersed phase in the rest of the oil.

In an oil with large molecules the viscosity, which is already large by itself, is further increased by the presence

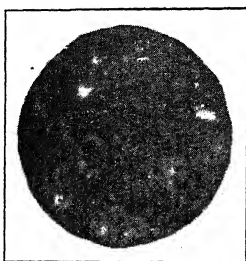


FIG. 15. A Photomicrograph of Cylinder Oil in Polarization Microscope.

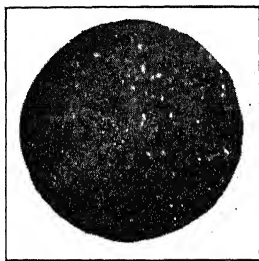


FIG. 15a. A Photomicrograph of Cylinder Oil Containing Resin, in a Polarization Microscope.

of colloidal suspensions. According to Einstein, the viscosity  $\eta_s$  of a colloidal solution, so-called sol, is

$$\eta_s = [1 + 2.5(\mu/\rho)]\eta_0$$

where  $\eta_0$  is the viscosity of the solvent and  $\rho$  the density of suspended particles, so that  $\mu/\rho$  is their volume per cubic centimeter. Such systems not only are very viscous, but also may possess some plasticity. (See Section 3.) It is quite probable that cylinder oils are not only highly viscous, but also plastic.

When an electric field is applied to a colloidal system, the particles, owing to their charges, travel to the electrode of the opposite sign. This phenomenon is known as cataphoresis. In oils it occurs only in extremely intense fields. We shall return to this subject in Section 11.

The relationships described above will be used in the discussion of dielectric losses in oils.

*Summary.*—Liquid systems which, besides the principal phase, contain also a second highly subdivided phase are generally called colloidal. They are classified into sols and gels according to whether the particles are separate or aggregated into a network. In addition to the heat motion, the particles are kept in suspension, because of solvation and an electric double-layer. Such particles cause a dispersion of incident light known as the Tyndall effect, and also produce luminous points in a polarization microscope. The more viscous an oil, the larger the amount of colloidal components. Colloidal oils are not only highly viscous, but often also plastic. The drift of suspended particles in an electric field is known as cataphoresis.

**7. Oxidation.**—As was mentioned in Section 1, the principal organic insulating liquids of practical importance are those which are chemically stable. Oxidation is the most frequent change which occurs in an organic substance, and its chemical and physical features will now be considered in more detail. This subject forms a chemical counterpart to the subject of Section 5, because there we were discussing changes due to a physical association with foreign substances. Here we shall explain changes due to a chemical effect.

As is well known, the basis of organic compounds is constituted by carbon atoms which are connected with the other atoms of a molecule by means of their four valence bonds. For the sake of simplicity, we shall at first disregard nitrogen, phosphorus, and other atoms of less frequent occurrence, and shall consider only hydrogen and oxygen. Beginning with compounds which contain hydrogen only, the so-called hydrocarbons, one always finds in them definite aggregated groups, such as methyl, methylene, etc. Such groups are attached to each other to form either an open chain or a ring, as has already been men-

many components with relatively small molecules, which are considerably above the point of solidification. On the other hand, a highly viscous oil contains components which are just above the point of solidification at room temperature, while some especially long molecular chains are already solid even at room temperature and therefore are precipitated as a dispersed phase in the rest of the oil.

In an oil with large molecules the viscosity, which is already large by itself, is further increased by the presence

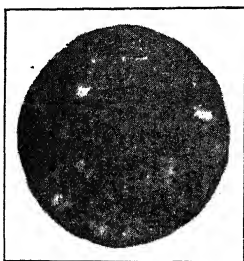


FIG. 15. A Photomicrograph of Cylinder Oil in Polarization Microscope.

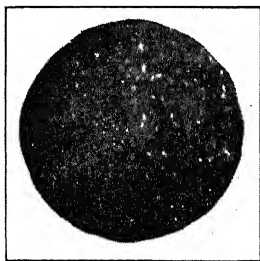


FIG. 15a. A Photomicrograph of Cylinder Oil Containing Resin, in a Polarization Microscope.

of colloidal suspensions. According to Einstein, the viscosity  $\eta_s$  of a colloidal solution, so-called sol, is

$$\eta_s = [1 + 2.5(\mu/\rho)]\eta_0$$

where  $\eta_0$  is the viscosity of the solvent and  $\rho$  the density of suspended particles, so that  $\mu/\rho$  is their volume per cubic centimeter. Such systems not only are very viscous, but also may possess some plasticity. (See Section 3.) It is quite probable that cylinder oils are not only highly viscous, but also plastic.

When an electric field is applied to a colloidal system, the particles, owing to their charges, travel to the electrode of the opposite sign. This phenomenon is known as cataphoresis. In oils it occurs only in extremely intense fields. We shall return to this subject in Section 11.



The relationships described above will be used in the discussion of dielectric losses in oils.

*Summary.*—Liquid systems which, besides the principal phase, contain also a second highly subdivided phase are generally called colloidal. They are classified into sols and gels according to whether the particles are separate or aggregated into a network. In addition to the heat motion, the particles are kept in suspension, because of solvation and an electric double-layer. Such particles cause a dispersion of incident light known as the Tyndall effect, and also produce luminous points in a polarization microscope. The more viscous an oil, the larger the amount of colloidal components. Colloidal oils are not only highly viscous, but often also plastic. The drift of suspended particles in an electric field is known as cataphoresis.

**7. Oxidation.**—As was mentioned in Section 1, the principal organic insulating liquids of practical importance are those which are chemically stable. Oxidation is the most frequent change which occurs in an organic substance, and its chemical and physical features will now be considered in more detail. This subject forms a chemical counterpart to the subject of Section 5, because there we were discussing changes due to a physical association with foreign substances. Here we shall explain changes due to a chemical effect.

As is well known, the basis of organic compounds is constituted by carbon atoms which are connected with the other atoms of a molecule by means of their four valence bonds. For the sake of simplicity, we shall at first disregard nitrogen, phosphorus, and other atoms of less frequent occurrence, and shall consider only hydrogen and oxygen. Beginning with compounds which contain hydrogen only, the so-called hydrocarbons, one always finds in them definite aggregated groups, such as methyl, methylene, etc. Such groups are attached to each other to form either an open chain or a ring, as has already been men-

tioned in Section 1. Such monovalent negatively charged groups or radicals, derived from the paraffin series by removal of one hydrogen atom, are called alkyls. Their general formula is  $C_nH_{2n+1}$ .

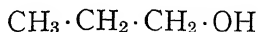
The question therefore is at which point of an organic molecule the oxidation, that is, the entrance of oxygen, takes place. Generally speaking there are two possibilities. If both fail, then that particular compound is thoroughly stable against oxidation.

The first possibility is that at a certain place in an organic molecule an oxygen atom is already present. As a general rule, oxidation more frequently proceeds from those points of a molecule where this process has already begun. Thus, beginning with hydrocarbons, the stability of compounds at first decreases. The further oxidation products are more and more unstable.

To give an example, the hydrocarbon propane has the formula



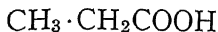
and is quite stable. Introducing an oxygen atom converts the molecule into one of alcohols which are not so stable. Two alcohols are possible. The normal propyl alcohol



is oxidized into propyl aldehyde

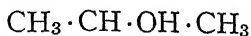


which can be readily converted into propionic acid



One readily sees that oxidation proceeds from a point at which it has begun.

The iso-propyl alcohol



is oxidized into acetone



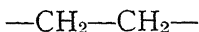
and the latter, with the separation of carbon dioxide, is further converted into acetic acid



The final product is always an acid, and acids are again comparatively stable against oxidation. Thus, beginning with a hydrocarbon, the stability at first decreases and then increases again, passing through a minimum for aldehydes and ketones. When an acid is further oxidized, its molecules are split, forming water and carbon dioxide; in practice this process may possibly take place in transformers.

We thus see that hydrocarbons are really the most stable compounds, because they contain no oxygen from which further oxidation can start.

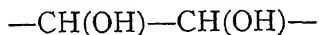
A second condition must also be fulfilled, namely, that no double bond should be present. Such bonds are points of easy attack. In hydrocarbons in which molecules form comparatively long chains, the group  $=\text{CH}_2$  is usually in the form



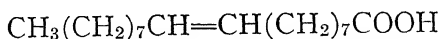
However, there are cases in which a group



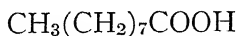
exists in the middle of the chain, indicating that two adjacent carbon atoms are connected by two valence bonds. Such double bonds possess the property of addition to a high degree; that is, one of the bonds readily opens up and becomes saturated with some outside atom, for example, a halogen. Hydroxyl groups also become easily attracted, so that groups of the form



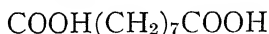
are produced. Now that there is a place in the molecule which contains oxygen, this place becomes further oxidized, and the molecule may even be completely disrupted, forming two acid molecules. As an example, oleic acid



may be cited. It is easily oxidized by opening the double bond and taking in two carboxyl groups. The result is pelargonic acid

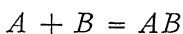


and the dibasic acelaic acid



The conclusion to be drawn is that in order to form stable insulating materials hydrocarbons must be as free as possible from double bonds.

Besides the molecular structure of a compound, certain physical factors are quite important. The process of oxidation, like any other chemical reaction, is governed by a constant which characterizes the velocity of the reaction. Let a reaction be symbolized by the equation:



and let the brackets below denote the degree of concentration; then we have the relationship:

$$d[AB]/dt = k[A][B] \quad (10)$$

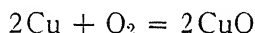
where  $k$  is the velocity constant.

The velocity constant increases exponentially with the temperature, so that at a high temperature the oxidation of an oil is very much accelerated. Equation (10) shows that the partial pressure of oxygen plays an important part. The significance of the temperature and partial pressure of oxygen is generally known, so that it seems superfluous to go further into this subject.

We shall now consider in greater detail three factors

which are of particular importance in the oxidation of organic liquids.

(a) The presence of some metals or of some other solid bodies often promotes oxidation. In all such cases a so-called catalytic action takes place. A foreign substance cannot produce a reaction which otherwise would not take place, but it may accelerate a slow reaction. The foreign substance participates in the reaction somewhat, but is always being regenerated, so that it is not a part of the final product. In our particular case, a foreign substance, usually a metal, attracts oxygen to itself and then gives it to the oil. In order to carry out such a cyclic process it is essential to use a metal which has two different stages of oxidation, or, as this is usually expressed, two different valences. Such a metal at first combines with an amount of oxygen sufficient to form the higher oxide, and then gives up part of it and is converted into the lower oxide. Copper is the most important of such metals, because it is both monovalent and divalent. First, it combines with enough oxygen to form cupric oxide, according to the formula



After this, cuprous oxide and atomic oxygen are formed, according to the formula



The latter is transferred into an organic substance with particular ease.

To some extent, iron and some other metals act similarly. Therefore the presence of copper in an oil is always dangerous, particularly at a high temperature. This fact is of great importance in cable and transformer engineering. (See Section 16.)

It is noteworthy that not only metals but also some other solids may be harmful. In this connection the following unpublished observations by the author may be

mentioned: If an oil be heated for several hours at about  $120^{\circ}\text{C}$  under identical conditions in two vessels, one made of glass and the other of enameled porcelain, a strong discoloration often takes place in the glass vessel, while the oil in the porcelain vessel remains practically unchanged. A discoloration is a rather reliable qualitative measure for oxidation, so that glass walls apparently exert an appreciable catalytic action which the porcelain enamel does not possess. This observation has not been followed any further.

(b) The above-described acceleration of a reaction is of chemical nature, but there are catalysts which may be called physical. In connection with the adsorption phenomena discussed in Section 2, it has often been observed that the presence of very finely divided substances promotes a chemical reaction. Such is the action of platinum black, which consists of extremely minute particles of platinum. It is usually assumed that the boundary surface is the active agent. The finer the subdivision the greater is the specific surface (surface per unit weight). It is known from experimental investigations that on such a surface gases are concentrated and adsorbed. Such adsorbed gases react considerably faster with other substances which are present than they do in the adjacent gas phase. This phenomenon is known as surface catalysis.

The mechanism of this process is probably a twofold one.

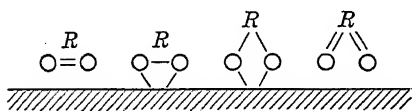


FIG. 16. Oxidation of an Organic Molecule by Activated Adsorbed Oxygen.

First, it is clear from equation (10) that a considerably increased partial pressure of the adsorbed gas (because the gas is more concentrated

near the boundary) must accelerate the reaction. Secondly, the gas molecules are apparently activated in a peculiar way by the adsorption forces which exist in that region. One may imagine (Fig. 16) that one of the bonds of an oxygen molecule is taken up by the surface to which it is

adsorbed, so that the stability of the whole molecule is reduced and it may combine with an organic radical  $R$  much more readily.

Such phenomena may occur also during the oxidation of an organic dielectric at a suitable boundary surface, although their occurrence is usually associated with an adjacent gas phase.

(c) A third possibility for the acceleration of oxidation lies in electrochemical processes. One needs only to visualize the processes going on in an electrolytic bath (Fig. 17). A source of voltage (a cell) is connected to two electrodes,  $A$  and  $K$ , which dip in a semi-conducting dielectric. When the current is flowing in the clockwise direction, the electrode at which the positive current enters the bath is called the anode, and the other, at which it goes out, is the cathode.

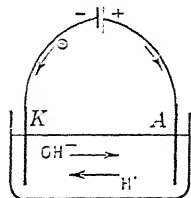
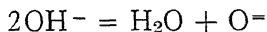


FIG. 17. Electrolysis.

In the metal conductors the current is due to the motion of electrons only, as is shown in the figure on the left-hand lead. These electrons collect at  $K$  and charge it negatively; they move away from  $A$  and therefore charge it positively. The anode is therefore always positively charged, and the cathode negatively charged.

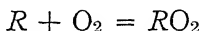
In an electric field thus produced in the bath, the ions travel to the corresponding electrodes (Section 8). It is mainly the negative hydroxyl ions,  $\text{OH}^-$ , which travel towards the anode, and the positive  $\text{H}^+$  ions which travel towards the cathode. If the organic liquid in the bath is absolutely stable against chemical reaction, the charges on the electrodes can cause no changes in it, and it takes no part whatever in the process. The  $\text{H}^+$  ions neutralize the cathode, combine into hydrogen molecules, and escape as hydrogen gas. The  $\text{OH}^-$  ions first undergo the reaction



Then the oxygen ions give up their negative charge at the

positive anode, are combined into molecules, and escape as oxygen gas.

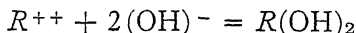
The phenomenon is different when the dielectric is not absolutely stable. Chemical reactivity goes hand in hand with the tendency to take up electric charges. An oxidation means an absorption of a positive charge; a reduction, an absorption of a negative charge. This follows from the equation ( $R$  = organic radical):



when one considers that oxygen often enters into a radical in the form of a negative ion. Thus the process of oxidation may be thought of as consisting in a radical's first becoming positive and then combining with an oxygen ion, as is schematically expressed by the equation



or



On the other hand, a radical must become negatively charged in order to combine with a positive hydrogen ion.

If some oxidizable substance is present it will become positively charged at the anode, and therefore oxygen ions will not combine into molecules and escape in gas form, but will combine with positively charged radicals. This is the mechanism of the so-called electrolytic oxidation. This process allows a rapid oxidation of intrinsically unstable substances if they may be made available in the liquid phase, or are adjacent thereto, for the reason that part of the oxygen in the liquid phase always exists in the form of ions.

The phenomenon just described takes place in a particularly clear form when the material of the anode itself is being oxidized. This is known as electrolytic corrosion. Organic liquids also are often oxidized in this manner, even though the process may not be followed so easily. It must also be kept in mind that it is not always an external



electromotive force which causes a current to flow. Consider two metal pieces which dip in a liquid and which are electrically connected on the outside; let these metals be quite far apart in the electrolytic potential series, as are copper and iron. A primary element is then formed in which the current within the liquid flows from the less noble metal (iron) to the nobler metal (copper). Oxidation takes place on the less noble metal. Such elements are called local elements. Their functioning requires an appreciable water content in the liquid phase.

*Summary.*—The applicability of organic liquids for insulation purposes depends primarily upon their stability against chemical changes, particularly oxidation. It is shown that primarily two conditions must be fulfilled in the molecular structure: (1) no oxygen in the original molecule, since oxidation progresses from a place where it has begun; and (2) absence of double bonds, because such bonds are readily broken and cause oxidation. The velocity of oxidation depends mainly upon the partial pressure of oxygen and upon the temperature; it increases with both. Besides, three other causes may accelerate oxidation, namely (a) admixtures of foreign substances, particularly of metals with multiple valence which act as catalysts; (b) boundary surfaces which act as adsorption agents, thus accelerating oxidation partly by causing a greater concentration of reactive groups and partly by activating the atoms; and finally (c) electrolytic processes which cause unstable radicals to be positively charged at the anode and thus facilitate their combination with oxygen or hydroxyl ions.

## CHAPTER IV

### ELECTRICAL AND OPTICAL PROPERTIES

8. **Conductivity with Direct Current.**—We shall now give a survey of the electrical properties of liquid dielectrics. The treatment cannot be as unified and systematic as in the preceding chapters, because the electrical properties are by no means so completely understood as the mechanical and thermal properties. For the present, any generalizations regarding behavior must be based on experimental data, because a secure theoretical foundation is still lacking. Considerable progress in this field has resulted from the investigations of K. W. Wagner and P. Debye, and recently in particular from those of J. B. Whitehead; we shall later refer more than once to the work of these investigators.

We shall first consider the phenomena produced when a continuous voltage is applied to a dielectric, because the processes are more simple than those with alternating voltage and in some respects are more fundamental. Let a voltage  $U$  be applied to a condenser of surface  $f$  and distance  $a$  between the plates; the resulting current,  $I$ , is determined by the equation

$$I = (f\sigma/a)U$$

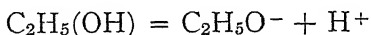
where  $\sigma$  denotes the conductivity, which is a characteristic quantity for a given liquid. For substances which obey Ohm's law,  $\sigma$  is independent of the applied voltage and therefore is a constant which characterizes that substance. The current is then always proportional to the applied voltage. If Ohm's law does not apply exactly, the rela-

tionship between  $I$  and  $U$  is not linear, and  $\sigma$  is not a constant. Measurements on liquid dielectrics show that they generally obey Ohm's law at comparatively low values of voltage gradient, but not beyond these. The boundary between the two ranges lies somewhere between 10 and 20 kV/cm.

When the voltage across a condenser is gradually increased, the current at first increases in proportion, and then beyond 20 kV/cm it begins to rise more rapidly. For practical purposes, values of potential gradients beyond this limit may be called *high-tension fields*. In accordance with our sequence of topics, we shall consider the latter range only briefly at this point, but shall discuss it in greater detail in Chapter V.

For the sake of completeness it should be mentioned that in some cases there is a third range between the above two, one in which the current increases more slowly than the voltage. This range corresponds to the so-called electrical saturation. With liquids, it may be clearly observed only when they are in an extreme state of purification. With gases, electrical saturation is a well-known phenomenon, which is due partly to the same causes, but also partly to others.

Let us consider first the range of low values of field stress within which  $\sigma$  is a constant. What is the cause of this conductivity? For dielectrics such as alcohols, which belong among semi-conductors, the question may be answered quite easily. These are substances which furnish their own ions. The fundamental phenomenon is electrolytic dissociation, by which a neutral molecule is broken up into a positive cation and negative anion. For example, for ethyl alcohol



The hydrogen ion is the cation, and the alcoholate is the anion. In this sense an alcohol is really a weak acid, as is proved by its compounds with alkali metals, for

example, potassium alcoholate. The number of free ions is a function of the concentration of the non-dissociated portion of the liquid, and for this phenomenon, as elsewhere in physical chemistry, the often-applied law of mass action holds true. Let  $c_m$  be the concentration of molecules,  $c_k$  that of cations, and  $c_a$  that of anions; we then have

$$(c_k \cdot c_a)/c_m = K \quad (11)$$

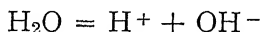
where  $K$  denotes the dissociation constant. The values of  $c$  are usually expressed in gram-molecules per liter. For pure alcohol,  $c_m$  is a constant and may be incorporated in  $K$ . We therefore have

$$c_k \cdot c_a = K'$$

The number of free ions ascertained in this manner determines the conductivity of a dielectric.

What is the situation with real insulating liquids? For example, benzene surely does not dissociate; a spontaneous dissociation, as it is called, does not exist. In this case there are three possibilities for conductivity:

(a) The most frequent case and the one which usually occurs in practice is that of a dielectric with some water content. Attention has already been called to this important point in Section 5. Water is dissociated according to the equation



and also follows the law of mass action. Let the concentration of water molecules be  $c_w$  and let the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions (evidently equal to each other) be  $c$ ; then

$$c^2/c_w = K_w$$

or

$$c = \sqrt{c_w K_w} \quad (12)$$

$c_w$  is usually a very small quantity. For example, if an oil contains 0.1% water,  $c_w = 0.001$ . For an insulating liquid

$K_w$  should be of the order of magnitude of  $10^{-25}$ , so that  $c$  is of the order of magnitude of  $10^{-14}$  (in mols per liter).

(b) A second possibility lies in the fact that an organic liquid in the presence of air is always more or less oxidized, as is explained in Section 7. The end-product of an oxidization is regularly an acid. But an acid is always dissociated into a hydrogen ion and an anion. It is then at once clear that a certain amount of conductivity is present. The acid will exhibit a definite dissociation constant, let us say  $K$ , so that if the concentration is  $c_0$  mols per liter, the concentration of ions is

$$c = \sqrt{c_0 K} \quad (12a)$$

From chemical determinations of the so-called degree of acidity (see Section 16)  $c_0$  may be estimated at  $10^{-3}$  and  $K = 10^{-21}$ , so that  $c$  is approximately equal to  $10^{-12}$ .

(c) There are some highly purified liquids whose water content is practically zero, and which are not at all oxidized (for example, hexane or benzene is thoroughly stable). In such dielectrics, current conduction may be measured only with the most sensitive devices, since the conductivity is of the order of magnitude of  $10^{-18}$  mho cm. In such cases conductivity is of photoelectric nature. Particularly penetrating rays, probably the so-called cosmic radiations, loosen electrons from the molecules, and these electrons cause electrical conduction. Radioactive admixtures may produce a similar action. When such a liquid is protected by a lead shielding which absorbs the incoming radiation the measured values of conductivity are still lower. On the other hand, the conductivity may be increased by subjecting the liquid to a source of light of high intensity. Liquids in such an extremely pure state are of only secondary importance in practice, because actual insulating liquids cannot be maintained in such a state.

We have thus indicated the various reasons for which a dielectric may contain a finite value of ion-concentration  $c$ . The next step is to show how to determine the con-

ductivity from the value of  $c$ . For this purpose the so-called molar conductivity of an electrolyte is used. Consider a plane condenser with the distance between the plates equal to 1 cm and the space between filled with an electrolyte, in such a way that there would be exactly 1 mol of free ions between the plates (that is, one gram-molecule by weight). The conductivity of such a system is called the molar conductivity because it is produced by exactly one mol. One cubic centimeter of the solution contains  $10^{-3} c$  mol ( $c$  is per liter, so that  $10^{-3} c$  is per cubic centimeter); hence the conductivity per cubic centimeter is

$$\sigma = \sigma_m 10^{-3} c \quad (13)$$

where  $\sigma_m$  denotes the molar conductivity.

For aqueous solutions,  $\sigma_m$  is of the order of magnitude of 100. It must be kept in mind that the mobility of ions (see below) is inversely proportional to the viscosity of the solvent. Thus for an oil of viscosity equal to 1 poise,  $\sigma_m$  would be equal to about 1. For light liquid dielectrics  $\sigma_m$  is also of the order of magnitude of 100. If for an oil  $c$  equals approximately  $10^{-12}$ ,  $\sigma$  is about  $10^{-15}$  mho/cm. The observed values of conductivity are of this order of magnitude; this to some extent is a proof that the foregoing numerical estimates are correct. Thus the existence of a conductivity for direct current at small values of voltage gradient will now be understood without further explanation.

As mentioned in the introduction, such a conductivity  $\sigma$  is quite characteristic for a given liquid dielectric. It may be placed side by side with the dielectric constant of the same substance and varies roughly in the same manner. We shall have something to say about this noteworthy parallelism in the next section, after we have discussed the nature of dielectric phenomena in more detail. A reasonable view of the relationship between  $\sigma$  and the chemical constitution of a compound has also been given in Section 1, and we refer the reader to that section. We

remind him again that by  $\sigma$  is understood that conductivity which manifests itself at comparatively small values of an electric field.

We shall speak further below about an essential limitation of the foregoing relationships, namely in connection with time as a factor. Another point, to be explained first, is variations of  $\sigma$  due to temperature. Such variations are quite considerable, as  $\sigma$  increases rapidly with increasing temperature, the relationship being an exponential one. We have

$$\sigma = \sigma_0 e^{-a/T} \quad (14)$$

or, for comparatively small temperature differences, approximately

$$\sigma = \sigma_0 e^{bt}$$

In accordance with the latter equation, when  $\log \sigma$  is plotted against the temperature in degrees Centigrade, an approximately straight line is obtained. The slope of this straight line is not the same throughout, but changes at a few places. In this respect the curve is of the same type as the viscosity curve discussed in Section 3.

Above room temperature, measurements of  $\sigma$  in terms of current and voltage are quite simple, the only apparatus required being a condenser and a sensitive galvanometer. Below room temperature the measurements are quite difficult, because as a rule the currents to be measured are exceedingly small. Because of the importance of such measurements we shall briefly indicate the method.

A suitable condenser for such measurements is shown in Fig. 18, in which  $a$  is a thick-walled glass vessel closed

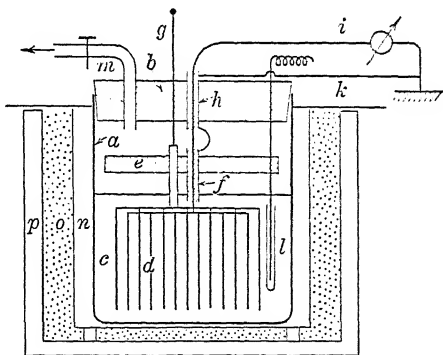


FIG. 18. A Measuring Condenser.

with a rubber plug *b*. Two sets of plates *d* are immersed in the oil *c* and are entirely separated from each other. The hard-rubber plate *e* holds the two sets together mechanically. One set of plates is connected to a metal rod *g* and the other to a wire which passes inside the metal tube *f*, filled with sealing-wax; this tube serves as a protection against creepage current along the surface of the oil and of the hard-rubber plate. The metal rod passes through the rubber plug, holds the hard-rubber plate and the two sets of condenser plates mechanically together, and also serves as lead for the voltage. The protected wire passes through the rubber plug inside the shield *h* and is connected to the measuring instrument at *i*. The shielding tubes *f* and *h* are grounded by means of the wire *k*. The tube *l* contains a thermoelement, and *m* is a glass tube which connects with the pump. It is necessary to evacuate the space above the oil, because otherwise the residual moisture would freeze to ice at low temperatures and then melt again at rising temperature and wet all the insulating surfaces, including the sealing-wax. To prevent a similar occurrence on the upper surface of the rubber plug it is advisable to pass a current of lukewarm air over it. Otherwise measurements at a rising temperature, which are particularly valuable, would be impossible.

Down to  $-60^{\circ}\text{C}$  a freezing mixture consisting of acetone and carbon-dioxide snow is satisfactory. The metal housing around the glass vessel consists of three concentric spaces. In the inner space *n*, adjacent to the glass vessel, is a thin layer of acetone, which is a relatively good conductor of heat and remains liquid down to  $-60^{\circ}\text{C}$ . The middle space *o* contains carbon-dioxide snow on the sides and on the bottom, while the outer space *p* should preferably be evacuated like a Dewar flask, so as to minimize heat losses.

Although the total air capacitance of such an arrangement may be as high as 200 cm (with a modified construction it may even be as high as 2000 cm), yet with applied



voltages up to a few hundred volts the currents are very small, so that a mirror galvanometer cannot be used as a measuring instrument. Of the various possibilities we shall here describe briefly the direct-current amplifier shown in Fig. 19. In this figure, *a* is an electron tube, which must be of special construction to satisfy various conditions. The insulation of the grid must be particularly good, and the lead preferably placed in an amber bushing; a high vacuum must be maintained, and in order to prevent ionization of the residual gas an anode voltage of a few volts should be used; in other words, a

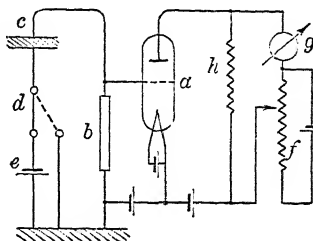


FIG. 19. Direct-current Amplifier.

double-grid tube is preferable, although it is not shown in the figure. The grid circuit contains a high resistance *b*, of the order of magnitude of  $10^9$  ohms. We shall explain below the best way of making such a resistor. The condenser shown in Fig. 18 is here indicated by *c*. By means of a double-throw switch *d* the condenser may be grounded, either directly or through a source of voltage *e*. The high resistance *b* is also grounded. When a small current flows through *c* and *b*, the voltage drop across *b* is added to the grid potential and therefore changes the anode current. A current of  $10^{-12}$  amp in *c* produces a drop of  $10^{-3}$  volt in *b*. If the "steepness" of the tube is  $10^{-4}$  amp/volt, this will give a current of  $10^{-7}$  amp, which may be readily measured on a galvanometer. The amplification is thus  $10^5$ .

In order to be able to use a mirror galvanometer in the plate circuit it is necessary to compensate for the anode current proper. For this purpose, a potentiometer *f* is connected in series with the galvanometer *g*, and is so set that in the zero position no current flows through the galvanometer. A resistance *h* of a few thousand ohms is connected in parallel with this branch, so that the plate current flows

through it. When the voltage  $e$  is switched in, an additional plate current (in the foregoing example  $10^{-7}$  amp) flows through the galvanometer, because it has a lower resistance than that of the shunted resistance  $h$ .

The above-mentioned high resistor  $b$  should preferably be of the liquid type. A satisfactory compound is obtained by dissolving picric acid in a mixture of ethyl alcohol and benzene. The more alcohol in the mixture, the lower the resistance. If phenol is added to the compound, the resistivity of the resulting product becomes practically independent of the temperature within the limits of  $10^{\circ}$  to  $30^{\circ}$  C.

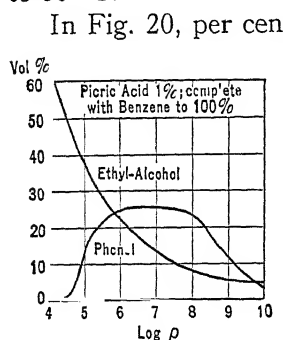


FIG. 20. Composition of Some Liquid Mixtures Used as Resistors.

In Fig. 20, per cent contents of alcohol and phenol, by volume, are plotted against values of resistivity  $\rho$ . The solution always must contain 1% of picric acid; the volume is completed to 100% with benzene. The ingredients used must be desiccated as far as possible. Knowing the form of the available container and the magnitude of the desired resistance, one may readily compute the value of  $\log \rho$ . Only platinum wires or screens should be used as electrodes. After being sealed in glass, such a liquid resistor will last indefinitely and remain quite constant. It may be recalibrated from time to time. Such resistors are also useful for various other purposes in high-voltage engineering. The upper voltage limit is about 1 kV/cm; the current limit varies with the voltage, and the output should not be greater than 1 watt/cm for glass tubes of 1- to 2-cm diameter; for 1 kV/cm this means a current of 1 milliampere. Such limitations are of course of no consequence in connection with the amplifiers described above.

Measurements performed with this arrangement on a

transformer oil give curves such as that shown in Fig. 21. This was a transformer oil which was overheated in the presence of copper so that the conductivity at room temperature was  $5.10^{-14}$  mho/cm, that is, about ten times as high as for an oil which has not been overheated. The curve consists of two approximately straight-line portions with a slight bend at about  $-10^{\circ}$  C. At lower temperatures the slope is about 60% higher than at higher temperatures.

A comparison of this curve with that of viscosity in oil (see Fig. 10) shows an evident resemblance between the two; even the numerical values of the slope to the right and to the left of the bend are similar. This is the reason for believing that the variability of  $\sigma$  with the temperature is principally a result of changes in the viscosity. Such is

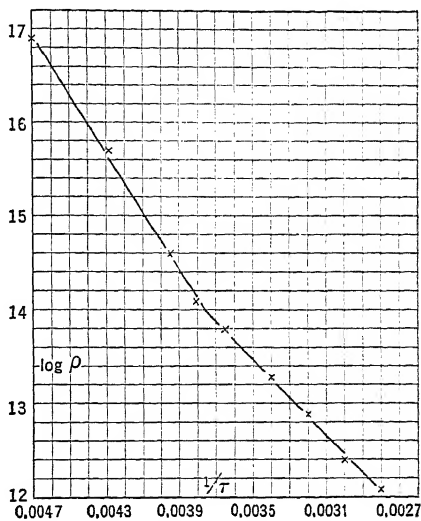


FIG. 21. Resistivity of a Transformer Oil as a Function of Temperature.

actually the case. We have seen that the conductivity may be computed as a product of the two quantities  $\sigma_m$  and  $c$ . But according to the definition,  $\sigma_m$  is the current within a mol in a unit field (1 volt/cm). On the other hand, the electric current is equal to the rate of flow of matter times its electric charge. The flow of matter, expressed in mols per second, is equal to the velocity of ions in a unit field. If this velocity is  $u$ , and the unit condenser contains 1 mol, then  $u$  mols per second pass through the boundary surface; in other words, the rate of flow of matter is equal to  $u$ . Let  $F$  ( $=96,540$  coulombs) be the electrical charge of an electrochemical equivalent, and let

$nF$  be the charge of a  $n$ -valent mol; then the electric current is

$$\sigma_m = nF(u + v)$$

where  $u$  is the so-called mobility (velocity in unit field) of the cations and  $v$  that of the anions. Stokes's law (see Section 3) holds approximately true for the motion of spheres in a viscous medium, so that the force of friction is equal to  $6\pi\eta ru$ , where  $\eta$  denotes the viscosity of the medium and  $r$  the radius of a particle. The driving force is  $n_i e$  volts per centimeter, where  $n_i$  denotes the valency of the ions and  $e$  an elementary electric charge; in other words, the mechanical force is equal to  $(n_i e/300)$  dynes. After the velocity of the ions has become constant, the electrical force is merely overcoming the frictional resistance to their movement; therefore the two forces may be equated, with the result that

$$u = (n_i e)/(1800\pi\eta r),$$

so that  $\sigma_m$  is inversely proportional to  $\eta$ , or, which is the same,  $\rho$  is directly proportional to  $\eta$ . This explains the similarity of the two curves plotted against temperature. Just as  $\eta$  increases at lower temperatures, so does  $\rho$ .

A more detailed comparison of the curves shows distinct numerical differences. Aside from the fact that the bend in the curve for  $\eta$  lies at  $+35^\circ \text{C}$ , and for  $\rho$  at  $-10^\circ \text{C}$ , the differential quotients are also different. To the left of the bend,  $d(\log \eta)/[d(1/T)]$  equals 2.3; to the right of the bend it is equal to 1.1; whereas  $d(\log \rho)/[d(1/T)]$  to the left of the bend is 3.2 and to right of it is 2.0. This means that the variations in viscosity are considerably smaller than those in the resistance; consequently, there must be a second reason for changes in the resistivity with temperature. This other reason is the second factor in  $\sigma$ , namely, the quantity  $c$ . It may be shown theoretically that the dissociation constant  $K$ , to whose square root  $c$  is proportional, also varies exponentially with the absolute

temperature. Therefore, a greater slope of the  $\rho$  curves as compared to  $\eta$  curves at once becomes clear. Expressed in words, the conductivity of an oil increases with increasing temperature (1) because the frictional resistance of the ions is reduced, and (2) because the number of ions increases, owing to a stronger dissociation.

A study of viscous oils with the arrangement shown in Fig. 18 yields interesting results. Because of low conductivities it is necessary to work with a condenser of about 2000-cm air capacitance. The curve in

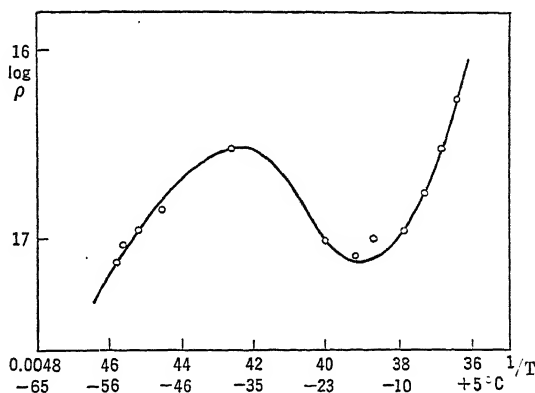


FIG. 21a. Resistivity of "Cable-Saturant Oil" between 0° and -60° C.

Fig. 21a\* shows the results of the author's measurements on a heavy oil (cable-saturant oil of the Texas Co.) of 140-poise viscosity at 20° C. It appears that in the range between -20° and -40° C the resistivity decreases with decreasing temperature. This peculiar result should first be confirmed by other experiments, because the measurements are somewhat difficult and contain possibilities of errors.

The following explanation may be given for this behavior: Solid particles distributed in the oil have a higher surface conductivity due to adsorbed ions. With decreas-

\* In this figure the numbers along the axis of ordinates decrease upward.

ing temperature these particles form aggregates, and their increased surface conductivity becomes more and more pronounced, causing an increase in the conductivity of the whole system. It is only below  $-40^{\circ}\text{C}$  that a normal decrease in conductivity takes place. In this manner, from the studies described above, some information may be gleaned as to the inner structure of an oil.

Having now sufficiently explained the concept of conductivity, we shall have to say a few words about the two other ranges, namely, those of saturation and of increasing conductivity. Until recently, saturation had been observed only by Joffé, in very highly purified hexane. Since that time, Whitehead and also Nikuradse, the latter working in Schumann's Institute, have succeeded in proving the existence of saturation in oils. A curve obtained by the latter author is shown schematically in Fig. 22.

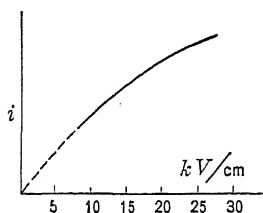


FIG. 22. Saturation Current in an Oil.

At a voltage gradient of  $20\text{ kV/cm}$  the current curve bends down. For an oil somewhat attacked by oxygen, Whitehead has found, at 750 and 1500 volts, the same current when the electrodes were 0.5 cm apart, but different currents when they were 1 cm apart. Nikuradse insists in particular that saturation takes place only with extremely well-purified oils. The author of this book could not detect saturation even with the most careful purification, using a distance of about 13 mm. It seems that besides as low conductivity as possible, a very small distance (a few millimeters at the most) is necessary for this phenomenon.

The reason for electric saturation in oils is similar to that for saturation in gases. There it is known from the phenomenon of glow discharge that saturation begins to take place when the number of charged carriers swept away per second by the current is equal to the number of those newly formed per second. Thus saturation is a

result of a finite rate of formation of new ions. In highly purified liquid dielectrics, charge carriers are formed only photoelectrically at a finite velocity; hence saturation occurs. However, saturation has also been observed in oils in which electrolytic conductivity is surely present. Hence it must be concluded that in a dielectric the formation of ions due to dissociation (which in an aqueous solution occurs almost instantaneously, owing to a high concentration) proceeds at a finite velocity, because the numbers of ions and of non-dissociated molecules are exceedingly small. This agrees with the observation that the phenomenon of saturation is the easier to produce, the more perfect is the desiccation, that is, the smaller the number of non-dissociated water molecules. By a more accurate study of such phenomena in oils, or preferably in dielectrics of more definite chemical constitution, it should be possible to determine the velocity constant of the breaking up of molecules into ions.

We shall consider the third range only briefly, because it is described in greater detail in Section 13. When the voltage gradient is raised beyond 20 kV/cm the current increases more rapidly than it would according to a straight-line law. This rising branch of the curve has been studied experimentally by a large number of investigators. The increase in the current is more and more rapid, and when the voltage has been sufficiently raised a breakdown takes place. The reason for this phenomenon is a rapid increase in the number of charge carriers, because of ionization through collision by swiftly moving ions.

We shall now consider in greater detail variations in conductivity with time, because of a recent interpretation of this phenomenon by Whitehead, which also throws light on the cause of dielectric losses in oils (see Section 9). Experience shows that when a direct voltage is applied to a dielectric, the current varies with the time, and generally speaking, decreases with it. One may then ask how conductivity could be defined in the sense described above,

since the current continually varies. A satisfactory answer to this question is not easy, and that is why it is difficult to obtain reliable numerical data on the subject.

A partially satisfactory answer is as follows: The most pronounced variations in the current take place within the first 5 minutes after an application of voltage. After this, the current becomes more nearly constant, although not absolutely so, and continues to decrease very slowly. The appearance of the phenomenon suggests that the changes within the first few minutes may be due to a different mechanism from that for the changes which take place later, although in reality both mechanisms surely overlap. Thus a relatively true value of conductivity may be obtained after a few minutes, and this value, with respect to the preceding phenomena, may be called the final conductivity. In accordance with a practical engineering rule, the current is measured one minute after the circuit has been closed, but the most recent investigations show that this interval of time is insufficient, because the current continues to decrease appreciably for several minutes.

It will thus be seen that the phenomena of conduction may be subdivided into rapid and slow changes. We shall consider them separately. More rapid phenomena are over after the first 5 to 10 minutes (theoretically, of course, after a much longer time), and are analogous to those observed in solid dielectrics. There the phenomenon is known as dielectric absorption. In a solid dielectric some electric charges actually penetrate into it, and therefore the initial current is quite high. After a sample of insulating material cannot absorb any more charges, we obtain the true conduction current. If the condenser is then discharged, the absorbed charges flow out only gradually; the observed discharge current of greater duration is equal to the difference between the charging current and the conduction current. The cause of dielectric absorption will be discussed in greater detail in the following



section, and we shall only mention here that it is primarily due to non-homogeneity in the dielectric. Joffé has succeeded in proving that in very highly homogeneous dielectrics absorption also takes place, by reason of a polarization of the substance itself.

Until recently no absorption phenomena, or only very slight ones, had been observed in liquid dielectrics. This seemed very plausible, because one could not very well imagine non-homogeneity of structure in a liquid in a normal state. It has only recently been established that the current possesses distinct characteristics indicative of absorption. Polarization has been proved to be the cause of this phenomenon. It only seems strange that practically no discharge currents have been observed.

Such absorption currents have been measured oscillographically by Whitehead and Marvin, who have obtained curves of charging currents of a shape shown in Fig. 23. They distinguish three portions of such a curve: a rapid drop within a few milliseconds, a constant current up to about 1 second, and then a current slowly decreasing to zero within, say, 30 minutes. After about 5 minutes the further changes are rather insignificant. A discharge current lasts only for the first few milliseconds and corresponds to the above-mentioned first part of the charging current; there is no corresponding discharge current for the two other parts of the curve of charging current.

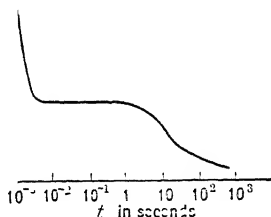


FIG. 23. Charging Current in Oil (after Whitehead).

That the observed shape of the charging current is due to a polarization within the liquid dielectric has been experimentally proved as follows. The distribution of potential at various places in a condenser was determined experimentally by means of probe measurements. Normally the distribution of potential  $\phi$  should be linear, as

shown by the dashed line in Fig. 24. Probe measurements showed, however, that after 10 minutes the potential distribution was according to the full-line curve; that is, the actual potential gradient (electric field intensity) at both electrodes was greater and in the middle of the liquid

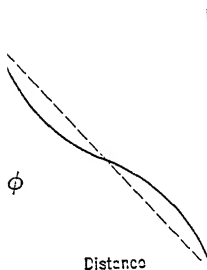


FIG. 24. Potential Distribution in Oil (after Whitehead).

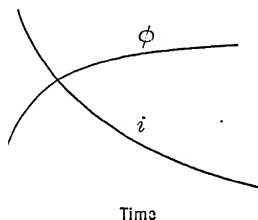


FIG. 25. Potential and Current Curves in Oil (after Whitehead).

lower than the average gradient. The building up of a non-linear potential distribution occurs during the same interval of time, during which the value of the current gradually drops. Parallel measurements on the same sample (Fig. 25) gave approximately the same variation with time at a given place for the potential  $\phi$  and the charging current  $i$ . The mutual dependence of the two quantities is thus clear.

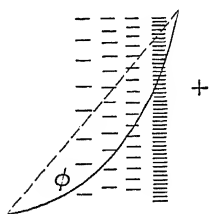


FIG. 26. Space Charges.

The next step is to explain the non-linear distribution of potential, its causes, and the reasons for ascribing it to polarization. Consider the condenser shown in Fig. 26; the straight dashed line of distribution of potential corresponds to a dielectric free of space charges. The first derivative of the potential, that is, the field strength, is then everywhere the same. Should a negative space charge be concentrated near the positive electrode, however, a correspondingly higher positive charge would

accumulate on the electrode itself; the field strength in the immediate vicinity of the electrode would become very high and would gradually decrease away from it. Since the total voltage must remain unchanged, the distribution of potential will be of a character shown by the full-line curve  $\phi$ . The actual curve for  $\phi$  (Fig. 24) shows that space charges in the dielectric accumulate at both electrodes. This concentration of charges is due to the electric field, which attracts anions to the anode and repels cations from it. Such a local accumulation of charges would be naturally equalized, owing to diffusion, but when the ionic concentration is quite low the diffusion proceeds too slowly, and such a stationary distribution of charges takes place that the electrical forces are slightly greater than the forces of diffusion; a current is thus produced compatible with the boundary conditions.

This separation of negative and positive ions is called polarization. It necessitates a corresponding increase in charges on the electrodes, and this explains the high initial charging current. The more nearly the polarized state approaches its final form, the lower the charging current becomes, until finally the true conductivity current alone is left. It will also be seen that our preceding considerations about conductivity strictly hold true only for a condenser free of space charges, but the approximation in most cases is sufficiently good, since space charges are not excessive.

Strictly speaking, the phenomena just described should also determine the discharge current. It is only after the space charges have been gradually equalized that

the bound charges of the electrodes may become free; therefore, the discharge current should last over a comparatively long interval of time. However, in contrast to the charging current shown in Fig. 23, Whitehead has found

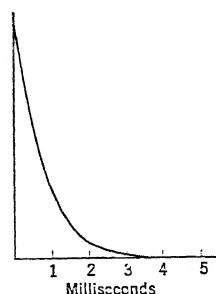


FIG. 27. Discharge Curve in Oil (after Whitehead).

only a very short discharge current (Fig. 27) which lasted merely a few milliseconds. This may be explained by assuming that the positive and negative space charges within the oil do not cancel each other, but that each space charge is annihilated by the adjacent charge on the electrode, so that no current needs to flow in the external circuit.

It will be shown in Section 9 that the process just described may also be partly responsible for dielectric losses in liquid insulation.

On the basis of the above measurements of potential distribution, Herzfeld has computed the mobility of ions in oil. He obtained a value of  $3.5 \times 10^{-6}$  (cm/sec)/(volt/cm); multiplying this value by the ratio of the viscosities of oil and water gives the mobility in water equal to  $1.2 \times 10^{-4}$ . According to a rule given by Lorenz, this signifies that the corresponding ion in oil is built up of 110 atoms. Hamburger gives the boiling point of this oil at  $290^{\circ}$  C, which corresponds to 45 atoms.

The author has also succeeded in proving directly the existence of the above-mentioned space charges in an oil, and in determining them semi-quantitatively. This was done by means of containers permeable to oil, which were placed directly in front of the electrodes. After removal of the electric field the containers were withdrawn from the oil as rapidly as possible, and their charges were measured ballistically. It has thus been shown that in front of each electrode a charge of the opposite sign is accumulated, quite as pointed out by Whitehead. According to the measurements, the space charge increases approximately in proportion to the applied voltage.

We shall now consider changes in the current which take place within intervals of time greater than a few minutes and which consist in a slow decrease in the magnitude of the current. Strictly speaking, this slow process cannot be separated from more rapid changes, because they overlap. The short-time phenomena have been shown

to be a result of polarization and accumulation of charges as the concentration of ions carried towards the electrodes becomes shifted. The resulting state is determined by the value of  $c$ , which is the concentration of ions in the body of the dielectric, and which itself is determined by the molecular concentration  $c_0$ . With high values of electric field strength a delay in the formation of new ions out of molecules leads to saturation. As the current continues to flow, the source of ions gradually becomes limited, and the concentration of molecules also decreases. A regular electrolysis sets in, and the electrolytic products are removed. As a result, the value of  $c$ , and also the current, decrease. A so-called electric cleaning takes place; the liquid gradually contains fewer and fewer ions and therefore becomes dielectrically more valuable. This process has been scientifically investigated more than once, but so far it has not been applied in practice because of a lack of commercially paying apparatus. It has also been often observed that after the current has been cut off the self-purified oil quite soon acquires the original conductivity. This is due to the ease with which oil absorbs traces of water from the surrounding medium. However, this cleaning process is essentially irreversible, whereas a polarization produces perfectly reversible changes.

*Summary.*—In a liquid dielectric the principal source of conductivity is an electrolytic dissociation of dissolved electrolytes; in extremely well-purified samples, photo-electric conduction may also take place. The quantity and the nature of electrolytes being known, the conductivity may be computed numerically. It increases rapidly with temperature, and measurements within wide temperature limits indicate a close connection with viscosity. At higher values of electric field-strength a range of electric saturation is reached; after that the conductivity increases very rapidly, owing to ionization. Conductivity also varies with time. A rapid decrease takes place within the first few minutes, as a result of a polarization within

the dielectric and of a rapid decrease in the charging current in connection therewith. As the current continues to flow, the liquid becomes electrolytically purified, and this causes a further slow decrease in the value of the current.

**9. Dielectric Constant, Index of Refraction, and Dielectric Losses.**—Having discussed in the preceding section the direct-current properties of liquid dielectrics, we now turn our attention to their alternating-current properties. In the former instance the characteristic quantity was the conductivity  $\sigma$ ; here we shall be interested in two other factors. The dielectric constant  $\epsilon$  has already been briefly considered in the introduction, especially in its relation to the chemical constitution of a liquid. We shall discuss here the variability of  $\epsilon$  as a function of some factors which determine the state of the liquid, and shall also return to the remarkable parallelism between the values of  $\epsilon$  and  $\sigma$ . We shall also introduce here a new concept: the dielectric loss, characterized by the so-called loss angle  $\delta$ , or by  $\tan \delta$ .

When an alternating voltage is applied to a condenser which contains a dielectric the current equation is not quite so simple as with direct current. Let the applied alternating voltage in the simplest case be represented by a sine wave, that is, let

$$u = U_0 \cos \omega t \quad (15)$$

where  $U_0$  denotes the amplitude of the voltage and  $\omega$  the so-called circular frequency. This frequency is defined by the equation

$$\omega = 2\pi\nu$$

where  $\nu$  denotes the frequency in cycles per second and

$$\tau = 1/\nu$$

is the duration of a cycle. At the instant  $t = 0$ , we find that  $u = U_0$ , that is, the voltage reaches its positive ampli-

tude (Fig. 28). With increasing time the voltage across the condenser decreases, becomes negative, passes through  $-U_0$ , and increases again. When  $t = \tau$  it will be seen from equation (15) that  $u = U_0$ , since  $\cos 2\pi = 1$ . Thus  $\tau$  is actually the duration of a cycle, and  $1/\tau$  is the number of cycles per second.

With the applied voltage between the condenser plates varying as described above, the current through the condenser may be resolved into two components. First of all, the dielectric possesses a conductivity; let it be denoted by  $\sigma_\omega$ . It must be emphasized that  $\sigma$  for direct

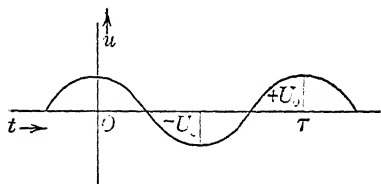


FIG. 28. Curve of an Alternating Voltage.

current is not identical with that for alternating current. Whereas the conductivity for direct current may at least approximately be denoted by a single symbol  $\sigma$ , here the conductivity at the frequency  $\omega$  is designated  $\sigma_\omega$ , to indicate that it is a function of the frequency. We thus have the so-called loss current,  $i_r$ , for whose instantaneous value we may write,

$$i_r = (fu\sigma_\omega)/a$$

Here  $f$  denotes the area of either set of plates and  $a$  the distance between them. Therefore  $i_r$  must vary according to a sine law, and we may write

$$i_r = [fU_0\sigma_\omega/a] \cos \omega t \quad (16)$$

This is expressed by saying that  $i_r$  is in phase with  $u$ , which means that for both quantities the positive amplitude, the zero values, etc., occur at the same instants.

The second component of the current is the so-called charging current. It does not really flow through the dielectric, but reaches only the metal plates and thereby charges the condenser. This component of the current is also sinusoidal, but not in phase with the voltage. The

current must lead the voltage because it is this current that charges the condenser, that is, produces the counter-electromotive force. When the voltage has just reached its positive maximum the current is being reversed, that is, it passes through zero; when the current passes through its negative maximum in order to produce a negative counter-electromotive force, the applied voltage is equal to zero. The current leads the voltage by a quarter of a cycle. A simple deduction shows that the charging current may be expressed by the equation

$$i_c = -\omega CU_0 \sin \omega t$$

where  $C$  denotes the so-called capacitance of the condenser. The capacitance of a condenser is defined as the ratio of an electric charge  $Q$  to the voltage  $U$ , between the plates, which produces this charge.

$$Q = CU$$

If air is used as dielectric, it is known from electrostatics that (in C. G. S. electrostatic units)

$$C = f/(4\pi a)$$

If the condenser is filled with another insulating substance,

$$C = (f\epsilon)/(4\pi a)$$

where  $\epsilon$  denotes the dielectric constant. We therefore have

$$i_c = -[(\omega f\epsilon U_0)/(4\pi a)] \sin \omega t \quad (17)$$

The dielectric constant  $\epsilon$  may be determined from this formula from measurements with alternating currents, and this is actually done in practice. Experimental evidence shows that  $\epsilon$  is not an absolute constant, as we have so far assumed, but varies with the frequency within more or less wide limits. When one speaks briefly of the dielectric constant of a substance, its limiting value at higher frequencies is usually understood. (See below.)

Not only  $\epsilon$  but  $\sigma_\omega$  as well is a function of the frequency,



so that the direct-current conductivity  $\sigma$ , discussed before, is only the limiting value of the conductivity at low frequencies. Whereas variations of  $\epsilon$  with the frequency are only moderate, the values of  $\sigma$  and  $\sigma_\omega$  usually differ by several powers of 10.

As a rule, not the quantity  $\sigma_\omega$  itself but the so-called loss angle is referred to. This is defined as the ratio of the amplitudes of the loss and charging currents. The name "loss angle" arises from the fact that  $i_r$  actually causes a liberation of heat within the condenser, as with a direct current, whereas the charging current, on account of a phase displacement of a quarter of a cycle, causes no heat loss. The name follows also from the construction shown in Fig. 29. Let  $I_r$  and  $I_c$  (the amplitudes of the two components of the current) be plotted as usual, perpendicular to each other—on account of a phase displacement  $\pi/2 = 90^\circ$  between the two; and let the diagonal of the resulting rectangle be  $I$ . Then the angle between  $I_c$  and this diagonal is the loss angle  $\delta$ . It will be seen from the figure that

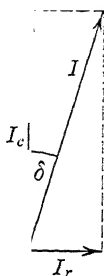


FIG. 29. Loss Angle  $\delta$ .

$$\tan \delta = (I_r)/(I_c) \quad (18)$$

For a small angle,  $\delta$  is approximately equal to  $\tan \delta$ , and therefore the quantity which is usually designated as the loss angle in reality is the tangent of this angle. Substituting the values of the amplitudes we obtain

$$\tan \delta = (2\sigma_\omega)/(\epsilon\nu) \quad (19)$$

$\sigma_\omega$  being expressed in C. G. S. electrostatic units. If in the first approximation  $\epsilon$  be considered as independent of the frequency, then at a constant  $\sigma_\omega$ ,  $\tan \delta$  should be inversely proportional to the frequency. In reality,  $\sigma_\omega$  depends to a great extent upon the frequency, so that quite a different law governs variations of  $\tan \delta$  with  $\nu$ .

After this short explanation of the concepts of dielec-

tric constant and loss angle, both as functions of the frequency, the available experimental material will now be explained on the basis of certain assumed kinds of mechanism which come into play. The treatment here given is quite brief, and the reader is referred to the author's book, *Elektrophysik der Isolierstoffe* (Berlin: Springer, 1930), where he will find a more detailed mathematical treatment of this subject. (Within the whole range of frequencies of interest to the dielectrician, the two above-mentioned quantities,  $\epsilon$  and  $\tan \delta$ , vary in a remarkably connected manner: within those limits where  $\epsilon$  is constant  $\tan \delta$  is generally very small, whereas within those limits in which  $\tan \delta$  has considerably greater values  $\epsilon$  always decreases with increasing frequency. The variability of  $\epsilon$  with the frequency is known as dispersion. Although throughout the above range  $\epsilon$  decreases with increasing frequency, such behavior is called anomalous dispersion, for the reason that within the purely optical range (not covered in Fig. 30), that is, with electromagnetic waves whose wavelength is of the order of

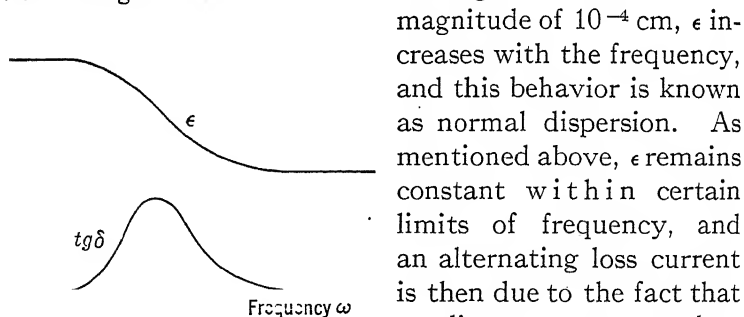


FIG. 30. Dielectric Constant and Loss Angle.

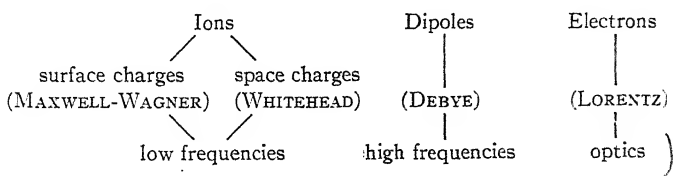
magnitude of  $10^{-4}$  cm,  $\epsilon$  increases with the frequency, and this behavior is known as normal dispersion. As mentioned above,  $\epsilon$  remains constant within certain limits of frequency, and an alternating loss current is then due to the fact that a direct-current conductivity  $\sigma$  is still present; since it is the value at zero

frequency, this conductivity may now be denoted by  $\sigma_0$ . It will be seen from equation (19) that if  $\sigma_0$  is of the order of magnitude of  $10^{-15}$  mho/cm, or about  $10^{-3}$  statmho/cm, and  $\nu$  is taken as equal to  $10^2$  to  $10^3$ , then  $\tan \delta$  lies within the limits  $10^{-5}$  to  $10^{-6}$ ; in other words, it is exceedingly small. Should a factor be present which causes much

higher losses, so that  $\sigma_\omega$  is considerably higher,  $\tau_\omega$  increases and is of the order of magnitude of  $10^{-3}$ . The dielectric constant always decreases neously with the increasing frequency. These rela shown schematically in Fig. 30.

The range of frequency within which  $\epsilon$  is variable is known as the dispersion range; it is also sometimes called the absorption range, because the electrical energy is partly converted into heat, owing to the loss component of the current.

What are the factors which cause absorption? They may be fundamentally subdivided into three large groups. First there may be a motion of ions, secondly a motion of so-called dipole molecules, and thirdly a motion of electrons inside a molecule. The first group of causes may again be subdivided into two sub-groups, namely, surface charges due to a lack of homogeneity within the liquid, and space charges. The first-group factors cause losses chiefly with alternating currents of low frequency, that is, within the so-called power frequencies and audible frequencies. A dipole action occurs with short electric waves, in other words within the so-called high frequencies, whereas motions of electrons become a factor with optical rays. Credit belongs to J. C. Maxwell and K. W. Wagner for an investigation of the first sub-group, and to J. B. Whitehead for the second sub-group; the second main group was investigated by P. Debye, the third by H. A. Lorentz. Thus the individual phenomena may be represented in the form of a table, as follows:



We shall now consider these three groups of phenomena in succession. For the first group it is assumed that an oil

is not a homogeneous liquid; this holds true in particular at lower temperatures and for those grades of oil which are highly viscous even at room temperature. That this assumption is fully justified has been shown briefly in Section 6. Although the detailed properties of the two

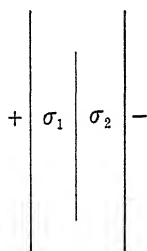


FIG. 31. A Two-layer Condenser.

components, the dispersed phase and the dispersion medium, are not yet known, it may safely be assumed that their electrical characteristics are not identical. In this theory it is postulated in particular that the values of their direct-current conductivity  $\sigma_0$  are different. The actual processes may be pictured by considering schematically two thin layers belonging to the two phases connected electrically in series (Fig. 31). Let the conductivities of the two phases be  $\sigma_1$  and  $\sigma_2$ ,

and let  $\sigma_1$  be greater than  $\sigma_2$ .

When a direct voltage is suddenly applied to such a system, at the first instant a greater current will flow through the layer 1 than through the layer 2, so that the boundary between the two will be positively charged. Accordingly, the field strength will be weakened in 1 and strengthened in 2, until the two currents are of the same value, and a steady state is established. Formally, the phenomenon is somewhat similar to the absorption current in the preceding section; the conductivity rapidly decreases with the time, and the dielectric constant of the system becomes relatively greater than at the beginning.

In this case the current decreases exponentially with the time, and the rapidity of decrease is determined by the so-called time constant, whose value  $\tau_0$  is as follows:

$$\tau_0 = \epsilon / [2\pi(\sigma_1 + \sigma_2)] \quad (20)$$

It is assumed in this formula that  $\epsilon$  is the same for the two phases. The time constant is defined as the interval of time during which an exponentially decreasing quantity (for example, a charging current) is reduced to  $1/e$  of its

original value, where  $e$  denotes the base of the natural logarithms. This particular effect has not been mentioned in the preceding section, because with direct current it occurs mostly with solid dielectrics. However, it also causes dielectric losses in oils which contain resin, in the following manner.

Assume that a condenser is subjected not to a direct voltage, as heretofore, but to an alternating voltage; then those large initial charging currents which modify the field distribution will occur at regular intervals. At low frequencies such periodic charging is of small consequence, because the current drops rapidly; but as the frequency increases this phenomenon leads to an appreciable increase in the average conductivity. At the highest possible frequencies the conductivity will be of the same magnitude as at the instant of switching in of a direct voltage; in other words, the value of conductivity approaches a definite limit as the frequency increases. So long as the duration of a cycle,  $\tau$ , is large in comparison with the time constant  $\tau_0$ , the conductivity remains low; however, when  $\tau$  is small in comparison to  $\tau_0$ , the conductivity has reached its final constant high value. Thus the most rapid changes of  $\sigma_\omega$  occur within the range of frequencies for which

$$1/\nu = \tau \text{ approximately equal to } \tau_0$$

What are the corresponding changes in the values of  $\epsilon$  and of  $\tan \delta$ ? Initially the dielectric constant has its value for direct current, corresponding to a high charging current. In proportion as  $\sigma_\omega$  increases, the corresponding charges are reduced, and in the limit they correspond to a purely capacitive charging. Thus within the range of frequencies for which  $\nu$  is approximately equal to  $1/\tau_0$ ,  $\epsilon$  gradually decreases from its high direct-current value  $\epsilon_0$  to a lower value which asymptotically approaches the high-frequency value  $\epsilon_\infty$ . For our simple schematic representation above we have

$$\epsilon_0 = 2\epsilon$$

because the layer 1 becomes practically free of electric stress, thus halving the distance between the plates. The final established value is

$$\epsilon_{\infty} = \epsilon$$

The value of  $\tan \delta$  increases with increasing frequency so long as  $\sigma_{\omega}$  also increases. When the latter becomes constant, then in accordance with equation (19)  $\tan \delta$  must begin to decrease. Thus the loss angle passes through a maximum within the range of values of  $\nu$  approximately equal to  $1/\tau_0$ .

Both  $\epsilon$  and  $\tan \delta$  may be represented as functions of  $\omega$ . For a schematic layer condenser, these two quantities depend not only upon  $\tau_0$  but also upon another factor,  $k$ , known as the absorption constant. For a two-layer condenser

$$k = [(\sigma_1 - \sigma_2)/(\sigma_1 + \sigma_2)]^2 \quad (20a)$$

When  $\sigma_1$  is considerably greater than  $\sigma_2$ ,  $k$  is nearly equal to 1. We further have:

$$\epsilon_{\omega} = \epsilon[1 + k/(1 + \omega^2\tau_0^2)] \quad (21)$$

Neglecting the pure conductivity for direct current on account of its small magnitude, we then have:

$$\tan \delta = (k\omega\tau_0)/(1 + k + \omega^2\tau_0^2) \quad (22)$$

These formulas show at once that the transition from the direct-current value to the high-frequency limiting value takes place in the so-called resonance range, characterized by  $\nu$  being approximately equal to  $1/\tau_0$ . Assuming the layer 1 to be semi-conducting, and thus  $\sigma_1$  approximately equal to  $10^{-11}$ , equation (20) gives  $\tau_0$  approximately equal to  $1/30$ ; that is, the losses due to the phenomenon under discussion occur at a low frequency.

It may seem somewhat strange to have assumed such high values of conductivity as those for  $\sigma_1$  above. However, with somewhat different expressions for  $\tau_0$  and  $k$ , the theory is also valid for a colloidal subdivision of one of the

phases. As is shown in Section 6, an adsorption layer containing electrolytes must then be assumed at the boundary of the two phases. Murphy and Lowry have demonstrated that Wagner's theory is also valid for such adsorption layers of higher conductivity. Accordingly, it is quite probable that a larger proportion of the losses in an oil containing resin is due to some such mechanism;  $\tan \delta$  may reach a value of the order of magnitude of a few one-hundredths.

Losses are also of measurable magnitude in pure transformer oils of moderate viscosity. In such oils deposits in suspension cannot be discovered with a polarization microscope, and the inhomogeneities, if they are present at all, are of ultramicroscopic size. Usually the losses are considerably smaller than in cylinder oils,  $\tan \delta$  being of the order of magnitude of  $10^{-4}$  to  $10^{-3}$ .

In such cases an ionic action may also take place, but not an accumulation of ions at the boundary surfaces; as has been shown by Whitehead, space charges may occur such as those described in the preceding section. He has proved oscillographically the existence of an initial high charging current with direct voltage. It is clear that with an alternating voltage the space charges must be built up anew each half-cycle, and therefore the losses must be higher. In this case the time constant equals several seconds and seems to be even higher than with boundary charges. Thus with this mechanism an alternating voltage of 60 cycles constitutes a high frequency, and the heat losses reach their limiting value at this frequency.

Whitehead also proved the truth of the foregoing assumptions quantitatively. For a particular oil he measured the initial current oscillographically; he also measured the loss angle by means of a Wien's bridge with triple amplification. The heat loss was computed from both sets of data, and the results were identical. The following table gives the results for a certain oil at three different temperatures and at an applied voltage of 1500 volts. The

data in the third column (values measured with 60-cycle alternating voltage) and in the fifth column (computed from direct-current values) are in excellent agreement.

Temp in °C	$\tan \delta$	Loss in watts	Initial current in amperes	Loss in watts
30	0.00015	$94 \cdot 10^{-6}$	$6 \cdot 10^{-9}$	$97 \cdot 10^{-6}$
45	0.00065	$407 \cdot 10^{-6}$	$269 \cdot 10^{-9}$	$404 \cdot 10^{-6}$
60	0.00165	$1031 \cdot 10^{-6}$	$683 \cdot 10^{-9}$	$1025 \cdot 10^{-6}$

The foregoing account does not cover the whole field. Tests have shown that dielectric losses may be quite high even in absolutely homogeneous thin liquids in which the above-described processes could not possibly take place. The existence of space charges also seems improbable, because these liquids are often quite rich in ions, which circumstance is rather unfavorable for the formation of space charges. On the other hand, all such dielectrics show the presence of dipole molecules.

By a dipole molecule is understood a molecule which as a whole is neutral at a considerable distance because the algebraic sum of its positive and negative constituents is zero, but in which the centers of mass of the positive and negative charges do not coincide. Such a molecule is shown in Fig. 32 at  $M$ , the magnitudes of the positive and negative charges being assumed to be equal. At a considerable distance such a combination acts like a neutral uncharged body, but not so in an immediate vicinity. Let  $A$  be a point charge which contains 1 unit of positive electricity. Let  $AB$  be the force of repulsion due to the positive charges in  $M$ , and let  $AC$  be the attractive force due to the negative charges in  $M$ . In its absolute magnitude  $AB$  is greater than  $AC$ , because the forces obey Coulomb's

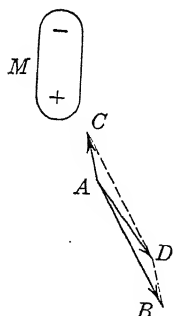


FIG. 32. A Dipole and a Point Charge.



law of inverse squares of the distance. The geometric sum of the two forces is  $AD$ , which is essentially a force of repulsion. A mathematical analysis shows that the resultant forces due to a dipole decrease inversely as the third power of the distance from the center of the dipole, that is, quite rapidly.

A dipole molecule is characterized by its dipole moment  $\mu$ , defined as the product of the charge  $e$  and the distance  $r$  between the centers of the charges of opposite signs. In other words

$$\mu = er$$

All molecules may be subdivided into two large groups, polar molecules and non-polar molecules, that is, dipoles and non-dipoles. The first group is by far the more numerous, in that most molecules have a dipole moment of finite magnitude, although its value varies greatly from substance to substance. The order of magnitude of  $\mu$  is a few  $10^{-18}$  absolute electrostatic units. The basic idea in Debye's dipole theory is the proof that the dielectric constant of polar substances in general is higher than that of non-polar substances, because dipoles contribute to the polarization. The word polarization is understood here in an electrostatic sense, meaning that an application of an electric field causes a dielectric to acquire an electric moment.

According to the elementary theory of polarization, the quantity  $\alpha$ , defined by the equation

$$[3/(4\pi)][(\epsilon - 1)/(\epsilon + 2)] = \alpha$$

represents the so-called polarizability of a dielectric; the product  $\alpha E$  is the electric moment per unit volume when a field of intensity  $E$  is applied. It used to be assumed that this polarizability was due to displacements of intramolecular electrons. (See below.) In reality, however, disregarding such phenomena as polarization by space charges,  $\alpha$  may be resolved into two parts, namely

$$\alpha = \alpha_e + \alpha_d, \quad (23)$$

where  $\alpha_e$  is ascribed to displacements of electrons, or of atoms within the molecules, and  $\alpha_d$  to dipoles. It is clear that polar substances must have a higher  $\alpha$  and therefore a higher value of  $\epsilon$ .

The mechanism of polarization by dipoles may be explained as follows. Owing to heat motions, the vectors of the moments of the individual molecules in a normal state lie in all possible directions, so that the resulting moment (from a considerable distance) is equal to zero. When an electric field is applied, the dipoles tend to place themselves parallel to the direction of the field, because in this position their potential energy is a minimum. Motions due to heat do not allow a permanent orientation of all molecules in the direction of the field, but a large number of molecules will tend toward this direction, so that a moment of finite magnitude comes into being. According to Debye

$$\alpha_d = (N\mu^2\rho)/(3MkT) \quad (24)$$

where  $N$  denotes Avogadro's number ( $6.06 \times 10^{23}$ ),  $\rho$  the density of the liquid at the absolute temperature  $T$ ,  $M$  its molecular weight, and  $k$  Boltzmann's constant ( $1.37 \times 10^{-16}$  erg/deg). It will be seen that  $\alpha_d$  increases as the square of the molecular moment  $\mu$  and decreases with increasing temperature.

The above-described orientation of dipole molecules takes place only with direct voltage or with alternating voltages of low frequencies, because of a finite velocity of orientation. By analogy with the time constant previously introduced in connection with charging of boundary surfaces, we shall define here a time constant whose order of magnitude is the same as that of the interval of time during which an orientation of a polar molecule takes place. The expression for the time constant of dipole orientation is

$$\tau_0 = (4\pi\eta r^3)/(kT) \quad (25)$$

where  $\eta$  denotes the viscosity coefficient of the liquid and

$r$  the radius of the dipole molecule. The more viscous the liquid, the larger the molecule, and the lower the temperature, the more slowly the orientation of the dipole takes place in any given field. With a low-frequency alternating voltage whose duration of a cycle is great compared to  $\tau_0$ , a complete setting takes place. At the other extreme, that is, at very high frequencies, for which  $\tau$  is small compared to  $\tau_0$ , the inertia of a molecule makes the amount of orientation negligible, so that at such frequencies  $\alpha_d$  must be put equal to zero. Thus  $\alpha_d$ , and consequently  $\epsilon$ , should generally decrease with the increasing frequency, their variations being mainly confined within the frequency range for which  $\nu$  is approximately equal to  $1/\tau_0$ . Thus the formal relationships are in general the same as before, only the mechanism of the phenomenon is quite different.

Let  $\epsilon_0$  be the value of the dielectric constant which corresponds to the total polarizability  $\alpha$  (with direct current). Let  $\epsilon_\infty$  be that which corresponds to  $\alpha_e$  alone (at high frequencies). We then have

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + \omega^2\tau_0^2)$$

The above-quoted formula for a two-layer condenser may be obtained from this formula by replacing  $\epsilon_\infty$  with  $\epsilon$  and introducing the value  $(1 + k)\epsilon$  in place of  $\epsilon_0$ .

Although the process of orientation in itself is rather unessential at very low and very high frequencies, it becomes of importance within the resonance range, in that the dipoles oscillate in synchronism with the applied field. Consequently the heat loss due to their friction becomes quite pronounced. The loss angle,  $\tan \delta$ , passes through a maximum and is expressed by the formula

$$\tan \delta = (\epsilon_0 - \epsilon_\infty)\omega\tau_0/(\epsilon_0 + \epsilon_\infty\omega^2\tau_0^2)$$

which also may be reduced to the form previously quoted. From a formal point of view there is a complete agreement between the two theories.

So far as the order of magnitude of  $\tau_0$  is concerned, a substitution of numerical values in equation (25) gives  $10^{-10}$  second. This corresponds to wavelengths of the order of magnitude of 1 cm, in other words, to very rapid electric oscillations. With larger values of  $\eta$  and  $r$ , the critical frequency  $\nu$  (equal to  $1/\tau_0$ ) is also shifted to lower values. Therefore one cannot lightly dismiss the fact that in oils for which  $\eta$  is quite high (see Section 3) and in which some molecules are quite large, the losses, according to Debye, take place at quite low frequencies. Kitchin, among others, is of the opinion that the low critical frequencies found by Debye are in agreement with the foregoing theory; whereas to us it seems more probable that such losses are caused by inhomogeneity within the oil and by space charges. We wish to emphasize the fact that the above-described processes do not represent conflicting theories, but only different kinds of mechanism all of which act simultaneously; this or that factor becomes preponderant, depending upon the conditions of the experiment and particularly upon the range of the frequencies used.

As to the influence of the temperature on dielectric losses, it will be seen from equation (25) that  $\tau_0$  varies considerably with the temperature, mainly because the viscosity is a function of the temperature. The time constant decreases with rising temperature, and consequently the critical frequency  $1/\tau_0$  increases rapidly. Therefore, when studying the losses at a constant frequency and variable temperature, it is found that the value of the loss passes through a maximum. At high temperatures the dipoles are oriented practically instantaneously; at low temperatures they are not oriented at all. The loss curve as a function of temperature may be expected to have a similar shape for the phenomena of charges on boundary surfaces, because the time constant there contains  $\sigma$  and decreases therefore also with increasing temperature. The time constant and variations in space charges with temperature are not yet well

known in detail. A curve of  $\tan \delta$  for a cylinder oil is shown in Fig. 33. The maximum lies somewhat below  $0^\circ \text{C}$ . A rapid rise above  $25^\circ \text{C}$  is caused by a considerable increase in the direct-current conductivity, which naturally affects the corresponding alternating-current losses, whereas its contribution to  $\tan \delta$  below room temperature is negligibly small, as has been previously mentioned. From this curve alone one could not very well decide which particular phenomenon causes the losses, because the shape of the curve is common to them all.

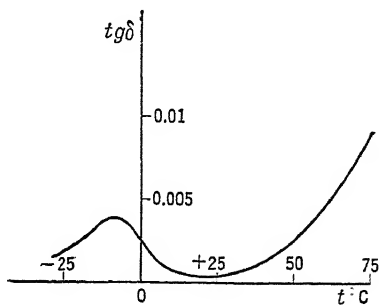


FIG. 33. The Loss Angle of a Cylinder Oil.

In conclusion a few words may be said about the phenomena within the molecules themselves. Lorentz in his classical electron theory assumed that the individual electrons were bound in a molecule quasi-elastically, and that they were capable of executing oscillations. Each electron is supposed to possess a natural frequency determined by the strength of the bond. Such electronic oscillations are supposed to be accompanied by radiation of electromagnetic energy, thus causing energy loss. Placed in an external electromagnetic field, these electrons are excited to oscillations, and as a result the molecules acquire an oscillating electric moment. This phenomenon is taken into account by the term  $\alpha_e$  in the formula for  $\alpha$ .

Any dielectric liquid, even a non-polar one, is supposed to respond in this manner, and it is for this reason that all dielectric constants are greater than 1. A detailed analysis shows that  $\epsilon$  slowly increases with the frequency, beginning in the optical range; this increase is called normal dispersion. According to Maxwell's relationship

the index of refraction  $n$  must also increase accordingly; this explains the higher refractivity of violet rays as compared with yellow and red.

Within definite ranges where an applied frequency happens to coincide with the natural frequency of an electron, a local decrease in the values of  $n$  and  $\epsilon$  takes place; this phenomenon is known as anomalous dispersion.

Within the range of visible light, dielectric losses are known as absorption of incident energy and are measured in terms of the so-called absorption coefficient. Although within normal ranges these losses are negligibly small, pronounced absorption bands occur in certain anomalous regions, with sharp maxima, because at such places the amplitude of oscillation of electrons is particularly great on account of resonance.

According to the quantum mechanics, an entirely different mechanism is pictured from that in classical physics, but the final results as to the variations in the index of refraction and in the absorption coefficient with the frequency are exactly the same.

Taking now all the considered frequency ranges together, it may be said that  $\epsilon$  decreases in steps, beginning with its direct current value  $\epsilon_0$ , the changes taking place where because of inertia (*a*) space charges cannot come into being, (*b*) boundary surfaces cannot be charged, and (*c*) dipole molecules cannot turn at the frequency of the applied field. At each of these characteristic places the curve for  $\tan \delta$  shows a "loss hump," whereas at other places its value is negligibly small. It is only in the optical range that the value of  $\epsilon_\infty$  (and also of  $n$ ) begins gradually to rise; by  $\epsilon_\infty$  we understand the value at high frequencies, that is to say, a minimum of  $\epsilon$ . This rise of  $\epsilon$  is interrupted at various places because of anomalous dispersion, in other words, absorption bands. This comprises the whole range from direct current up to ultraviolet rays. It would lead us too far to consider here the X-ray region or the Raman and Comp-

ton effects, the treatment in this book being more from the point of view of practical electrical engineering.

It should also be mentioned that the experimental curves which give values of  $\tan \delta$  as a function of  $\omega$  often have regions in which  $\tan \delta$  is approximately independent of  $\omega$ ; this seems not to be consistent with our theory, which permits only "humps" of  $\tan \delta$ . However, it must be remembered that often the individual fundamental processes overlap, and in this way the curves are considerably flattened.

The question of the parallelism between  $\sigma$  and  $\epsilon$  in dielectrics, mentioned in Section 1, is still to be considered. Nernst has already established the law that liquids with a high value of  $\epsilon$  possess a high dissociation ability for electrolytes; that is, their dissociation constant  $K$  is relatively large. It will be seen from formula (12a) that for such substances the ion concentration  $c$  and consequently  $\sigma$  must be correspondingly large.

Nernst's empirical law has become particularly clear since the establishment of the dipole theory. It has been shown that a high value of  $\epsilon$  is due to the presence of dipoles. All such compounds as nitrobenzene, ethyl alcohol, etc., which have high dielectric constants, also possess large dipole moments. The dipoles of the solvent orient themselves radially around the individual ions, being directed by the electrical forces of these ions. In this manner they bind their true charges and diminish their free charges. The attractive forces between the ions are weakened in this way, and dissociation is made easier. The remarkable relationship between dielectric constant and conductivity thus becomes intelligible.

*Summary.*—The concepts of dielectric constant and of loss angle are explained as functions of frequency. Then follows a description of various kinds of assumed mechanism which cause dielectric losses and at the same time a reduction in the value of the dielectric constant: (1) electric charges on boundary surfaces in liquids of colloidal

structure, for example, in a heavy mineral oil; (2) formation of space charges due to a finite velocity of electrolytic dissociation and diffusion; (3) orientation of dipole molecules in the direction of an electric field; (4) oscillation of electrons within atoms. These four phenomena become of importance in this order as one passes from low through high to optical frequencies. The dipole theory also explains the connection between the conductivity and the dielectric constant of liquid dielectrics.

**10. The Kerr Effect.**—Since the dipole theory discussed in the preceding section has been successfully applied to the explanation of the Kerr effect, the latter may be briefly sketched here. The inclusion of the Kerr effect may also be warranted since Carolus has introduced it into the technique of television and sound films, so that it is of more general interest to the electrical engineer.

The Kerr effect is the electric double-refraction observed in some substances, particularly liquid dielectrics, and noted first by Kerr. The details are as follows: As already indicated in the preceding section, rays of light are electromagnetic vibrations of very high frequency, so that formally they follow high-frequency oscillations in the same manner in which the latter follow currents of ordinary commercial frequencies, the frequency becoming higher and higher. With the highest frequencies it is customary to use the wavelength  $\lambda$  in place of the frequency  $\nu$ ; we have

$$\lambda\nu = c$$

where  $c$  is the velocity of propagation of the waves (in vacuum  $3.10^{10}$  cm/sec). The order of magnitude of wavelengths of visible light is  $10^{-5}$  cm (corresponding to  $\nu$  approximately equal to  $10^{15}$ ).

When a ray of light passes through different substances the frequency  $\nu$  remains unchanged. Only the velocity of propagation and consequently  $\lambda$  are modified. The



notation  $c$  is reserved for the velocity in vacuum; for other media we shall write

$$\lambda v = v$$

The wavelength in vacuum will be denoted by  $\lambda_0$ ; it reaches its maximum there; in various other media it is always smaller ( $\lambda < \lambda_0$ ).

The ratio  $c/v$  or  $\lambda_0/\lambda$  is denoted by  $n$  and called the refractive index. (See Section 9.) It is generally greater than 1. As is known from optics, the refractive index  $n$  is also equal to the ratio  $\sin \alpha / \sin \beta$ , where  $\alpha$  denotes the angle of incidence (the angle between the incident beam and the normal to the surface) and  $\beta$  the angle of refraction; hence the name—refractive index. Thus it is a reduction in the velocity of the ray which causes refraction.

In Maxwell's relationship mentioned above,  $n^2 = \epsilon$ , the value of  $\epsilon$ , strictly speaking, should correspond to the actual frequency of the light used. However, no appreciable error is committed if the value of  $\epsilon_\infty$ , that is, the one corresponding to high frequencies, is used in this formula, especially since the relationship itself is only approximately true. This relationship follows from the electromagnetic theory of light and indicates that the immediate cause for the lowering of the velocity of the propagation of electromagnetic waves is a change in the strength of the electric field due to a polarization of the dielectric. The explanation of the polarization given in the preceding section also furnishes a basis for the theory of refraction in optics.

Such being the case, a similar explanation should be sought for double refraction. In double refraction, which occurs in a number of crystals, the incident beam of light is split into two emerging beams. One of them obeys the law of refraction ( $\sin \alpha / \sin \beta = \text{constant}$ ), that is,  $n$  remains the same in all directions. This ray is called the ordinary ray. The other ray does not obey the law of refraction, and  $n$  is different in different directions. This ray is known as the extraordinary ray.

In most so-called uniaxial crystals (quartz, Iceland spar) the refractive index of the extraordinary ray,  $n_e$ , may be represented by an ellipsoid of rotation (Fig. 34). A

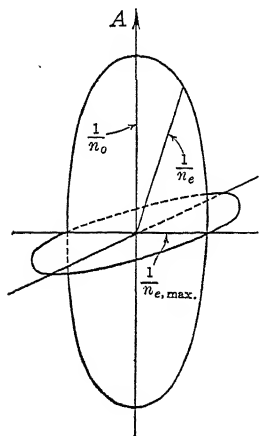


FIG. 34. Ellipsoid of Rotation of Refractive Index.

radius vector drawn from the center in a direction parallel to that of a ray of light gives the reciprocal of the refractive index  $n_e$  in that direction; in this particular case the ellipsoid happens to be a prolate spheroid. The major semi-axis gives the reciprocal of the ordinary refractive index,  $1/n_o$ . It will be seen that in such a crystal a particular direction, the so-called principal axis  $A$ , is optically and also crystallographically distinct from all others. It may also be mentioned that crystals for which the spheroid is prolate are called positive, whereas those for which the spheroid is oblate are called negative.

The nature of double refraction may be better understood by considering the direction of polarization of the two rays (optical polarization is not to be confused with electrical polarization). As is well known, a ray of light consists of electric oscillations which may take place in any direction perpendicular to the direction of the propagation of the ray itself. The fact that there are always also magnetic oscillations co-ordinated with the electric oscillations, in the sense of being perpendicular both to the electric vector and to the direction of propagation, is of no interest to us here. These electric vectors which oscillate according to the sine law may always be resolved into two mutually perpendicular components. For this purpose two mutually perpendicular planes are imagined in space which intersect each other along the direction of the beam of light, and each electric vector is resolved into components which lie in these two planes. In this manner the treat-

ment becomes independent of various directions of oscillation and one has only to consider two components which are independent of each other, and which always oscillate along a straight line in the same direction. Such a beam of light with electric oscillations along a definite direction is known in optics as a plane-polarized beam; it will thus be seen that any natural beam may be resolved into two mutually perpendicular plane-polarized components. The orientation of the two co-ordinate planes is just as arbitrary as are, for instance, the directions of the three axes of co-ordinates in resolving the motion of a molecule into its three components.

If the two rays of light emerging out of a crystal be analyzed by a suitable method, they will be found to be polarized in mutually perpendicular directions. Thus the splitting of the ray is due to the fact that the value of  $n$ , and consequently that of the dielectric constant of the medium, are not the same for different directions. Moreover, the direction of electrical oscillation in the ordinary ray is always in a plane perpendicular to the principal axis  $A$ . Thus, in this one direction, among an infinite number of possible directions, the medium has singular physical properties. In any direction perpendicular to  $A$  the values of  $\epsilon$  and  $\alpha$  are the same, and to these values there corresponds an exponent  $n_o$ ; a ray with such oscillations is propagated quite normally.

In terms of a chosen ordinary ray the direction of oscillation of the extraordinary ray is also given, this direction being perpendicular to the direction of oscillation of the ordinary ray and to the direction of the extraordinary ray itself. This direction of oscillation always forms a finite arbitrary angle with  $A$ . When the oscillation happens to be in the direction of the  $A$  axis, so that the ray itself is propagated normally to it (Fig. 34), the refractive index has its maximum value. This means that the molecules are more susceptible to electrification in the direction of the principal axis, and consequently  $n$  has a maximum in this

direction. These two limiting values,  $n_o$  and the maximum value of  $n_e$ , are called the principal refractive indices. For negative double-refracting crystals the limiting value of  $n_e$  is a minimum. When the direction of oscillation is at a finite angle to  $A$ , the ability to be electrified lies somewhere between the two limiting values and is graphically expressed by the corresponding length of the radius vector of the ellipsoid.

Thus the whole phenomenon is caused by a lack of symmetry in the molecules. With so-called isotropic bodies,  $\alpha$  is the same in all directions, but such is not the case with crystals of the above-described kind. With positive crystals the molecules are most easily electrified in the direction of the principal axis, and consequently  $\alpha$  in that direction is a maximum. Perpendicular to this direction  $\alpha$  has its smallest value, and the other values lie in the intermediate directions. Mathematically speaking,  $\alpha$  is a tensor.

How is it then possible for the phenomenon of double refraction to be observed in liquids which are typically

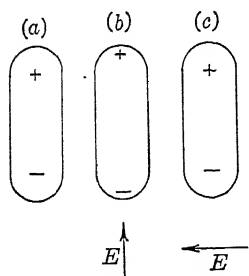


FIG. 35. Polarizability of a Dipole Molecule.

isotropic because of a random motion of their molecules? It must be granted that the molecules of most liquids are in themselves non-isotropic. We have seen that dipole molecules exhibit quite a large uniaxial asymmetry. Fig. 35 illustrates a dipole molecule in its normal state, at (a). Now let an external electric field  $E$  be applied, first in the direction of the dipole axis (b) and then in

a direction normal thereto (c). It is reasonable to assume that the additional moment  $\alpha E$  will be much greater in the first case than in the second, because the molecule may be much more readily deformed in the direction of the dipole axis than in a perpendicular direction.

In a neutral state the dipole axes are distributed in all

possible directions, and therefore this asymmetry is not noticeable. However, when a strong unidirectional electric field is applied, the dipoles become largely oriented in the direction of the field, as is discussed in the preceding section. Such a liquid then becomes similar to a crystal in which an orderly structure is due to the auxiliary valences of the molecules. In a polar liquid an external electric field acts as a directing agent. Such a liquid becomes more strongly polarizable in the direction of the electric field than in a direction normal thereto; consequently an incident beam of light becomes split into two beams, an ordinary and an extraordinary one, exactly as explained before. This is the explanation of the electric double-refraction in liquids, discovered by Kerr. The principal axis always coincides with the direction of the orienting electric field.

On the basis of such a picture, electric double-refraction may be correctly treated mathematically. The theory is due to Langevin; we shall give here only the results. Let  $n_e$  be the value of the extraordinary principal refractive index of the liquid in a field  $E$ , that is, the maximum of all values of  $n_e$ ; let  $n_o$  be the ordinary principal refractive index, so that  $n_e - n_o > 0$ . Let  $n$  be the refractive index of the liquid without the field and let  $\epsilon$  be the dielectric constant, so that  $\epsilon$  is at least approximately equal to  $n^2$ . Consider a dipole molecule of moment  $\mu$ , and in accordance with Fig. 35, let the polarizability of the molecule in the direction of  $\mu$  be denoted by  $\alpha_\mu$ , and perpendicular to it by  $\alpha_\mu^-$ ; then  $\alpha_\mu > \alpha_\mu^-$ , and if  $\alpha$  is the polarizability of the molecule for zero field, we have

$$(n_e - n_o)/n = [(n^2 - 1)(n^2 + 2)/(2n^2)] \frac{[(\theta_1 + \theta_2)/\alpha][(\epsilon + 2)/3]^2(E^2/2)}{(26)}$$

where

$$\theta_1 = [1/(45kT)][2(\alpha_\mu - \alpha_\mu^-)^2]$$

and

$$\theta_2 = [1/(45k^2T^2)][2\mu^2(\alpha_\mu - \alpha_\mu^-)]$$

Here  $k$  denotes Boltzmann's constant, and  $T$  the absolute temperature. It will be seen that the finite value of the difference  $n_e - n_o$  is caused by the quantities  $\theta_1$  and  $\theta_2$ , and that these latter are determined by the difference  $\alpha_\mu - \alpha'_\mu$ . It is of interest to note that even without a permanent dipole moment, that is, in case  $\mu = 0$ , the quantity  $\theta_1$  is different from zero. This is due to the fact that when the polarizability  $\alpha_\mu$  is different in different directions, even in the absence of a permanent dipole, a molecule becomes oriented in a direct-current field, with its axis of maximum polarizability in the direction of the field. Thus an asymmetric structure of the liquid is produced in this case as well.

An essential feature of the result is that the Kerr effect increases as the square of the applied field strength. Kerr himself established this fact experimentally. The factor by which  $E^2$  is multiplied in equation (26) is denoted by  $K$ . The order of magnitude of  $K$ , as computed from this equation, comes out to be about  $5 \times 10^{-12}$  abs. The same order of magnitude is found experimentally; for example, for ethyl alcohol  $3.3 \times 10^{-12}$ , for acetic acid  $17.8 \times 10^{-12}$ , for benzene  $1.5 \times 10^{-12}$ , and so forth. Since the refractive index  $n$ , as well as  $\theta_1$  and  $\theta_2$ , varies with the wavelength in accordance with Section 9, the constant  $K$  must also be subject to dispersion. One can see from equation (26) that approximately ( $h$  is a proportionality factor)

$$K = h(n^2 - 1)^2/n$$

This relationship is known as Havelock's formula, having been established by him empirically.

Besides equation (26), the foregoing theory also gives

$$(n_e - n)/(n_o - n) = -2$$

This relationship was verified experimentally by Pauthe-  
nier.

We shall limit ourselves here to the foregoing brief explanations. The Kerr effect will be considered in

somewhat more detail in Section 18, where we treat of its applications in television and in sound films.

*Summary.*—In a substance which possesses the property of double refraction there is a particular direction in which the polarizability  $\alpha$  is a maximum or a minimum; the corresponding refractive index is called the extraordinary principal refractive index  $n_e$ . Electromagnetic oscillations perpendicular thereto correspond to the ordinary refractive index  $n_o$ . An uniaxial asymmetry may be produced in a liquid by the application of an electric field; this causes electric double-refraction, the Kerr effect. The dipoles orient themselves in the direction of the field, and this produces an asymmetry in the polarizability. The magnitude of the effect is measured by the difference  $(n_e - n_o)$ . The magnitude of the Kerr effect may be deduced theoretically, and the results check well with the experimental values. The effect itself is proportional to the square of the applied electric intensity. The factor of proportionality depends upon the wavelength of the electromagnetic waves passing through the liquid.

## CHAPTER V

### BEHAVIOR IN INTENSE FIELDS

**11. Motion Phenomena.**—In this account of the subject of motions let it be first mentioned that only those motions are described which are an immediate consequence of an applied field of high intensity. There are also other motions which, though taking place in an intense field, are due to a different cause. Such a cause usually is a temperature rise in the dielectric. We shall return to a case of this sort in greater detail in Section 15, under "breathing" of high-tension cables. Heat streams in transformers are described in Section 16, and motion of oil in circuit-breakers in Section 17. All these motions are caused either mechanically or thermally and have nothing to do directly with an intense electric field.

The motions caused by an electric field may be subdivided into two groups, direct or electrical motions and indirect or mechanical motions. By a direct motion is meant one where an electric force is applied directly to the liquid which is being displaced; thus the driving force here is of electrical nature. With an indirect motion the electrical force is first converted into mechanical, so that the dielectric which is being displaced is acted upon by a mechanical force.

The first group of motions may again be subdivided into three sub-groups, according to the electrical state of the liquid. First, if the liquid is perfectly neutral, we have a purely dielectric action of the force. This sub-group may therefore be called dielectric displacement. Second, if the liquid is externally neutral, but possesses some separate



internal charges, motions of the carriers of these charges may take place in the opposite directions. In Section 6 such separate charges were named double-layers, and therefore such a motion may be called a displacement of double-layers. Third, if the liquid possesses an excess electrical charge even when considered from the outside, the external electrical force acts upon such a space charge (Section 8), and the liquid simply moves with it. This third sub-group is therefore called motion due to space charges.

We shall now briefly describe these four groups of motions.

1. *Dielectric displacement*, the first mentioned, is based on the general principle that a dielectric body placed in a non-uniform field tends to move to regions of higher field intensity. When a dielectric is polarized the potential electrical energy is thereby reduced. A system always tends to assume a position in which the potential energy is a minimum; consequently, a dielectric substance is drawn to places with higher field intensity because the polarization is greater there. The magnitude of the force per unit volume in any direction  $x$  may be computed from the formula

$$K = (\alpha/2)(\partial E^2)/(\partial x) \quad (27)$$

where  $E$  denotes the field intensity and  $\alpha$  the polarizability. The same kind of forces act in liquid dielectrics. Usually a motion of the liquid brings into play some other forces, so that an equilibrium is established in which all the active forces are balanced.

In a liquid such an opposing force is that of gravity. In high-voltage apparatus immersed in oil it is often observed that on live metal parts with considerable curvature the oil creeps up, overcoming the force of gravity. Of course another force, that of surface tension, also plays a part here. Because of surface tension the oil has a tendency to creep up even without an electric field.

According to Section 2, the rise along a vertical wall is given by the equation

$$h = \sqrt{[(2\gamma)/(\rho g)](1 - \sin \theta)}$$

where  $h$  denotes the rise,  $\gamma$  the surface tension,  $\rho$  the density,  $g$  the acceleration due to gravity, and  $\theta$  the boundary angle. When it is desired to compute exactly the rise in oil due to an applied field, all the three forces must be taken into consideration.

Quantitatively the phenomenon may be conveniently investigated in the experimental arrangement shown in Fig.

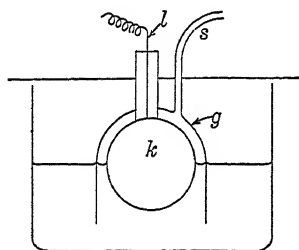


FIG. 36. Measurement of Dielectric Motion.

36. The main part of the apparatus is a metal sphere  $k$ , which is half immersed in oil and is covered air-tight with a glass bell  $g$ , from which a tube  $s$  leads to a pressure gauge. One pole of a source of high alternating voltage is attached to the lead  $l$  of the sphere; the other pole is grounded. The whole apparatus must be set up at a considerable distance from

other grounded conductors in order to have as simple relationships as possible.

When the oil is drawn up along the sphere it compresses the air within the bell, and the increase in pressure may be read on the gauge. The magnitude of the effect may also be computed theoretically. For an increase in pressure,  $\Delta p$ , with the voltage  $U$ , we have

$$\Delta p = kU^2 \quad (28)$$

where  $k$  depends in a definite manner upon the dimensions of the apparatus and the constants of the oil used. For transformer oil, with the radius of the sphere equal to 2.75 cm and a distance between the sphere and the bell of 0.6 cm,  $k = 4.2 \times 10^{-4}$ , when  $U$  is expressed in kilovolts

and  $\Delta p$  in millimeters of alcohol. A theoretical curve and some experimental points are given in Fig. 37. Such an arrangement may also be used as a direct-reading high-tension voltmeter, but only for alternating voltages. (See below.)

Still more striking is an arrangement in which the sphere is slightly raised above the oil surface. When a voltage is applied the oil rises appreciably, and when the voltage is increased a column is formed which touches the sphere. When the voltage is reduced the top of the column becomes separated from the sphere at quite a definite value of the voltage.

Deformation of droplets of water emulsified in oil also belongs in this group of phenomena; it will be considered in Section 14.

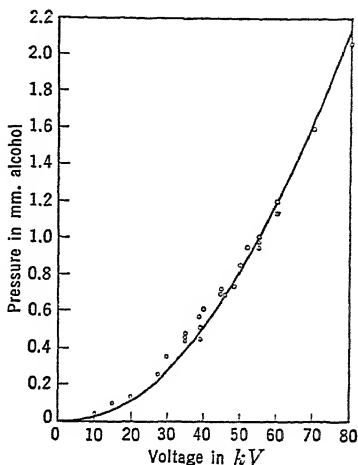


FIG. 37. Some Measured and Computed Values of Motion in Oil.

The curve follows the equation  $p = 3.3 \times 10^{-4} U^2$ . The little circles represent the experimental points.

2. A *displacement due to double-layers* requires first of all the existence of such double-layers. They come into being where two phases have a common boundary, and are due to two causes. First, a thermodynamic cause: like any dissolved substance, an ion between two phases possesses a so-called distribution coefficient, that is, the ratio of concentration in the two phases, generally speaking, is constant. When an electrolyte is dissociated into two ions which have a different distribution, evidently one of the phases must become positively charged and the other negatively charged. Secondly, double-layers may arise because of adsorption, as is briefly explained in Section 6. It is mentioned there that such double-layers may lead to

cataphoresis. When the separating surface between the two phases happens to lie in the direction of an applied field, the two phases are displaced relatively to each other. When one of the phases is dispersed in the liquid in the form of small particles, the particles are set in motion, and this phenomenon is known as cataphoresis. On the contrary, when one of the phases is in the form of a solid canal or a solid network which contains a liquid, the liquid is forced to move through the solid phase, and this phenomenon is known as electro-endosmose. This is quantitatively described by Helmholtz's equation, according to which the velocity of displacement

$$u = (\epsilon E \zeta) / (4\pi\eta) \quad (29)$$

where  $\epsilon$  denotes the dielectric constant of the liquid,  $E$  the intensity of the applied field,  $\zeta$  the difference of potential between the two phases, and  $\eta$  the viscosity of the liquid. Thus the dielectric must be non-homogeneous in order to make such a phenomenon possible, and it must contain finite numbers of ions to allow a so-called  $\zeta$ -potential to build up. This phenomenon takes place only in a direct-current field; with alternating voltage a permanent displacement would not be possible, but at the most only an oscillation.

Cataphoresis may be observed, for example, when water is emulsified in an organic dielectric. Fibers and lint suspended in oil also drift in an electric field, unless they are too dry. This drifting is often used for purification of liquids. For example, an oil may be improved cataphoretically by applying an electric field to it; of course an electrolytic cleaning also takes place simultaneously. Similarly nitrobenzene becomes purified in a Kerr cell.

Droplets in oil usually carry positive charges and therefore drift toward the cathode. According to Coehn's empirical rule, a substance with a higher value of  $\epsilon$  is, generally speaking, positively charged with respect to a

substance with a lower value of  $\epsilon$ . This rule has been verified in many cases, though not in all.

Endosmose is a motion of a liquid in a system of tubes when a potential difference exists between the liquid and the walls of the tubes. Helmholtz's equation holds true in this case also.

An example of electro-endosmose appears in the electrical resistance of fibrous insulating materials. Evershed has found that their resistance decreases with increasing voltage, in accordance with the equation

$$R = k/\sqrt[n]{U}$$

where  $k$  is a constant and  $n$  is approximately equal to 2. The reason for this phenomenon is as follows: A fibrous insulating material always has a capillary system which contains air and moisture. The air bubbles are surrounded with a thin film of water whose thickness determines the insulation resistance of the system. When an electric field is applied, the water, being charged positively with respect to the fibers, is carried towards the cathode; the water therefore is drained from the anode and forced into the thin water film, so that the film becomes thicker. The electric resistance is thereby reduced. After the applied voltage has been removed, the air bubbles gradually assume their former shape. The above explanation in this form is not quite satisfactory, but the author is not aware of a more rigorous theory. This phenomenon may be observed directly under a microscope on an artificial model consisting of capillary glass tubes.

3. *Motion of space charges.* Space charges which arise because of polarization have been discussed in Section 8. There is also another kind of space charge which is often observed in oils: the oil acquires a space charge of the same kind as the adjacent electrode. This kind of charge is always produced when an oil is connected in series with some better insulator, for example, air, paraffin, porcelain, etc. In such cases the oil plays the part of a semi-conduct-

ing extension to the adjacent electrode and therefore acquires part of its charge.

The existence of such space charges may be proved directly by means of the following arrangement: Some oil is poured into a glass vessel covered with paraffin on the outside; the vessel is placed on a metal plate, and a metal sphere is suspended in the oil. A direct voltage is applied between the sphere and the metal plate; then the voltage is removed. By discharging the insulated vessel, with the aid of a metal ring against the ground, through a ballistic galvanometer, one always obtains a discharge of the same kind as the charge on the immersed sphere.

An example of the motion produced by such charges is offered by the above-described arrangement in which a spherical electrode is placed above the oil level. If instead of alternating voltage a direct voltage is applied, the oil rises at the first instant, as with alternating voltage. However, after a short interval of time the oil becomes charged with electricity of the same kind as the electrode and is again repelled from it. Sometimes oil may also be observed to rise in the middle in the form of a fine stream, being dielectrically attracted, and fall down from the sphere in the form of small drops.

4. Motions of the group named above as *mechanical* or *indirect motions* are brought about in the following manner. When an applied field intensity exceeds the ionization limit of the air layer adjacent to oil (see Section 13), ions will be produced which perform an oscillating motion in an alternating field, a motion which is also transmitted to molecules of oil. The layer of ions oscillates in the direction of the field, and at every second half-cycle communicates a mechanical impulse to the oil. The layer of ions itself oscillates, but the adjacent neutral molecules on the surface always experience impulses in one direction only and therefore move away from the ionized layer. The force acting upon them is of mechanical nature, and therefore this motion may be called an indirect one.

Because of this so-called electric wind, splashes or mechanical wave motions sometimes take place on the surface of oil. The surface waves in oil in the vicinity of high-tension parts, so well known to high-voltage engineers, are due to such mechanical impulses, although other causes may also be active at the same time.

This kind of motion may be very strikingly demonstrated with the sphere arrangement mentioned above. As the alternating voltage is raised higher and higher a limit is reached beyond which the oil begins to splash and makes a steady equilibrium impossible; this limit depends upon the diameter of the sphere.

*Summary.*—There are the following possibilities of motion within a liquid dielectric under the influence of a high-voltage field: (1) Oil may be drawn to regions in which the electric field strength is higher, by purely dielectric causes. This motion may be studied with a sphere apparatus described in detail. (2) Motion due to double-layers: cataphoresis of small particles in suspension, or a motion of the liquid itself through a canal system (electro-endosmose). (3) An oil which contains a space charge may be directly accelerated by an electric field. (4) Ionized air acts mechanically as an electric wind upon an adjacent layer of oil and causes motions within it. Motions due to heat are discussed in Chapter VI.

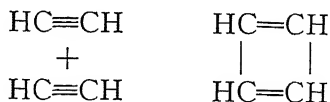
**12. Chemical Changes.**—In addition to the purely mechanical phenomena discussed in the preceding section, chemical changes may also take place in a liquid dielectric through the application of a high-voltage field. Such changes are fundamentally different from the simple oxidation discussed in Section 7. An oxidation is produced because of contact with air and because of heat, whereas the changes which are now to be described do not require either.

It must be clearly understood that an electrostatic field by itself cannot produce a direct chemical change. If an oil could be subjected to a high voltage under abso-

lutely perfect conditions, no chemical changes would take place in it. Numerous experiments have shown that for such changes it is absolutely necessary to have traces of gases. Such small amounts of gases as usually exist in the form of minute bubbles may be considered to be insulating layers in series with the liquid. There must therefore be within them a definite voltage drop which is usually sufficient to ionize the gas. This means that ions and electrons impinge upon the neutral molecules of gas with such force that the molecules are also broken up. Because of this so-called ionization by collision (for details see Section 13) more and more ions and electrons are produced, which impinge upon the adjacent liquid with a considerable kinetic energy.

A number of chemical reactions are initiated by such electronic bombardment. Thus, strictly speaking, it is not the static field itself, but the secondary electronic collisions, which lead to chemical changes.

Two types of reactions must be considered. One type is called polymerization; it consists in a straightforward combination of two or more molecules into a higher complex molecule, without giving off any by-products. One of the best-known examples is the polymerization of acetylene,  $C_2H_2$ , under the influence of a high-voltage field, to molecules of higher weight, at first liquid and later even solid. The reaction which takes place between two molecules may be written as follows:

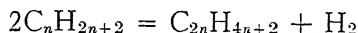


The triple bond is opened, and the two molecules combine. One may imagine an impinging electron causing another electron to be ejected from  $C_2H_2$  and combined with another molecule. The two molecules whose neutral state has thus been disturbed (one made positive, the other negative) combine into a double molecule. Phenomena of this



nature occur also in oils, especially in those of naphthene base. They also occur frequently with unsaturated compounds, as is shown by the preceding example.

Another typical reaction is known as condensation; it consists in a combination of two or more molecules with a simultaneous liberation of substances of low molecular weight.\* With oils such a by-product is mainly hydrogen gas. Such reactions take place in oils of paraffin base. The general formula for the constituents of such an oil is  $C_nH_{(2n+2)}$ . When two such molecules are combined the reaction is



and a hydrogen molecule is liberated.

Electrically the phenomenon probably consists in the knocking out of a positive hydrogen ion from a molecule by an impinging electron; the negatively charged remainder of the molecule then combines with a second neutral molecule, which at the same time gives up a hydrogen atom. The two hydrogen atoms thus liberated combine into a molecule.† The essential feature of the reaction is that by collision with electrons, molecules are broken up into ions of short duration which re-enter into chemical combinations. The reaction, being endothermic, requires energy, and this energy is supplied by the bombarding electrons.

Such phenomena occur in practice in high-voltage cables. As will be shown in Section 15, it is very difficult to avoid the formation of air pockets in a cable. When the applied voltage is sufficiently high, ionization sets in in such

\* Two types of reaction seem here to be combined into one. The first type is a decomposition reaction in which hydrogen is split off the parent oil molecule; the second type is strictly a polymerization or condensation reaction through carbon atoms, with the formation of the material of higher molecular weight.—Translator's Note.

† Another possible explanation is that the polymerization here results from the combination of two organic radicals resulting from the effect of an electron on two neutral molecules; during which process hydrogen is split off, the resulting radicals react together, and a polymerized molecule results.—Translator's Note.

pockets, and the adjacent layers of oil are bombarded by electrons.

Both kinds of reactions pictured above take place in a cable, the result being that highly polymerized substances are formed in oil. Initially these products are liquid; then



FIG. 38. Natural Wax Taken Out of a Cable.

they become solid; when the bombardment has continued for a sufficiently long time, they form a wax-like substance, often called X, although now this name is hardly justified. Such a wax is formed in the shape of shiny scales. The ratio of carbon to hydrogen is higher in it than in the original oil, which is a proof that condensation reactions have taken place. Whereas

oils themselves are readily soluble in benzene, such a wax cannot be dissolved in any organic solvent. A photomicrograph of such a wax is shown in Fig. 38.

Our knowledge of these substances is due primarily to the investigations of Hirschfeld, Meyer, and Connell, and likewise to those of Schoepfle and Connell. They have also brought out the fact that hydrogen gas is formed during these reactions.

It is important that methods for the artificial preparation of such products of condensation should be made available. First, on the basis of some observations by Losanowitsch, a sort of ozonizer may be used. He has found that when such an ozonizer contains gases, for example water vapor and carbon monoxide, or hydrogen and carbon dioxide, formaldehyde,  $\text{H}\cdot\text{COH}$ , is formed, which is later converted into solid substances. The silent discharge in the ozonizer furnishes electrons and therefore may cause polymerization of organic compounds. An

arrangement on this principle is shown in Fig. 39. It consists of two coaxial test tubes (1) and (2) with a piece of cork between at the bottom and some cylinder oil (3) above. Either mercury or water may be used as electrodes, both on the inside and on the outside; the leads are denoted by (4) and (5).

When such an arrangement is subjected to an alternating voltage of ordinary frequency, causing a field intensity of about 5 kV/mm, and the voltage is allowed to act for a sufficiently long time, products are separated out of the oil which are not soluble either in benzene or in alcohol. However, the method has several drawbacks. In the first place, the yield is very small. Second, the results are not easily reproducible. Third, some air must be mixed with the cylinder oil because it is only then that a corona discharge and condensation can take place. Such an experiment does not succeed with an oil from which all air has been removed. Moreover, a strong glow discharge also causes secondary carbonization, so that the light-colored condensates are contaminated by the darker products of combustion.

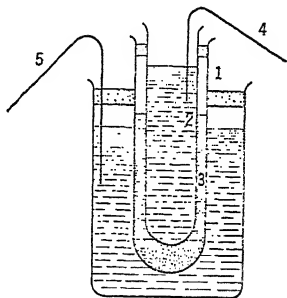


FIG. 39. Ozonizer for Oils.

For these reasons the above-described method is unsuitable for accurate investigations, although it is simple and may be sufficient for preliminary tests.

The efficiency may be considerably increased by increasing the frequency of the applied voltage and reducing the gas pressure. The electron stream is a quantity which for each half-cycle depends upon the voltage and drops rapidly with the time (similarly to the formation of space charges, Section 9); therefore, the electronic current must increase with the increasing frequency, at least up to a certain limit. Hence higher frequencies must be favorable

for the chemical reaction. Since the mean free path, and consequently the kinetic energy of the electrons, increases considerably with decreasing pressure, lowering the gas pressure is also favorable for the reaction.

The arrangement shown in Fig. 40 is quite satisfactory. A glass bell (1) with a ground edge is placed on a metal support (2). Inside the bell is a flat vessel (3) filled with oil. In the oil are placed two metal electrodes (4), with a spacer between, which in the simplest case consists of porous paper which becomes thoroughly saturated with oil. The lower electrode is connected with the support by means of the conductor (5), and a voltage is applied to the lead (6).

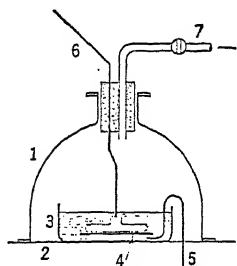


FIG. 40. Ozonizer for Oils under Reduced Pressure.

The glass tube (7) with a stopcock leads to a pump and a vacuum gauge. Usually one works at a pressure of a few centimeters of mercury, an electric stress of 5 kV/mm, and a frequency of 100 kc. With transformer oil, positive results are obtained after a run of a few hours, both electrodes becoming covered with a thin layer of wax. The reproducibility of the

results and the yield are considerably better than with the method previously described. Since air is present to a very limited extent only, carbonization phenomena are minimized.

It is of interest to note that it is impossible to force a chemical transformation in a highly viscous cylinder oil by using such relatively simple devices. Such oils are by far more stable than thin oils.

Perhaps the best method for an artificial chemical change in a liquid dielectric by means of electronic bombardment has been described by Schoepfle and Connell. It consists in the use of a Coolidge tube with a Lenard window which permits electrons accelerated in a very high field and endowed with the highest possible velocity

to be obtained outside the tube. The great power of such cathode rays to cause certain chemical reactions is well known from other experiments. Condensation was thus produced in oils which was entirely similar to the products of reactions which take place in cables, except that the reaction proceeded much more rapidly in the laboratory.

A modification of this method may be mentioned which consists in placing the oil under test in a discharge vessel, thus avoiding the use of the very expensive Coolidge tube. A vessel which may be used for such a purpose is shown in Fig. 41. The central spherical part, made of glass, has two ground joints. The bottom joint has a connection for water cooling and carries a platinum cap (1), sealed in and connected to the metal lead (2). The upper joint contains a hot cathode (3), with a protective cap (4) to prevent a scattering of electrons. There is also a side connection which leads to a high-vacuum pump.

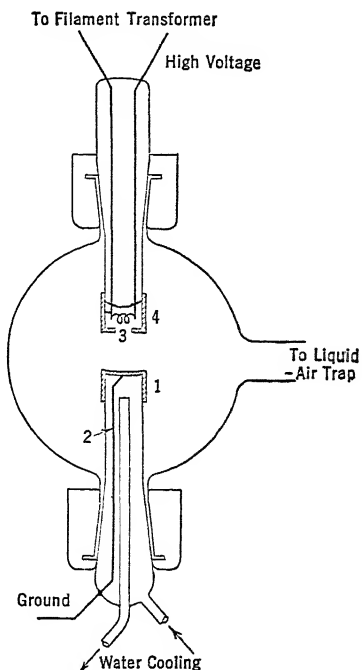


FIG. 41. Vessel for Subjecting Oil to Electronic Bombardment.

Some highly viscous mineral oil is placed on the platinum cap, the space is evacuated to a very low pressure, and the oil vapor is kept out of the vacuum pump by means of a low-temperature trap. By applying a voltage of a few kilovolts between the lower cap and the hot filament, quite a considerable increase in pressure is observed. If the pressure before the application of the voltage was,

say,  $10^{-10}$  mm of mercury, as measured by a 20- to 30-mm high adhering mercury column in a McLeod gauge, it rises to  $10^{-4}$  mm. If the voltage remains applied the pressure again drops to  $10^{-5}$  mm, but does not drop below this value.

This increase in pressure is an indication of gas development during the reaction. When the voltage is first applied, the oil on the platinum cap begins to boil vigorously, which also indicates a

formation of gas.

It seems that the transformation proceeds at a relatively high rate. Only a few minutes of bombardment are required to convert some oil into wax. As time goes on the reaction proceeds, even though a layer of wax formed on the surface of the oil somewhat protects the liquid underneath against electronic bombardment.

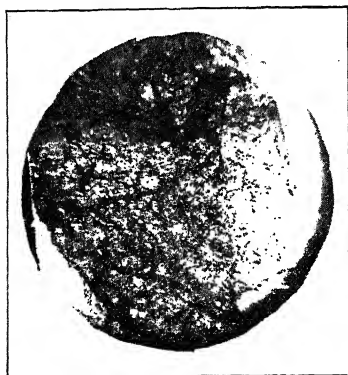


FIG. 42. Artificial Wax Formed after a Three-minute Electronic Bombardment in High Vacuum.

A photomicrograph of artificial wax produced by electronic bombardment is shown in Fig. 42. It will be seen that it is quite similar to the natural product shown in Fig. 38.

*Summary.*—Under the influence of a high-voltage field, liquid dielectrics undergo chemical changes. These changes are polymerization, which is a combination of molecules without the formation of by-products, and condensation, which consists in a combination of molecules with a simultaneous formation of hydrogen gas or other substances of low molecular weight. These chemical reactions are caused not by the field itself, but by the impinging electrons of high energy which are produced by ionization by collision in the adjacent gas phase. In practice the most important reaction is the conversion of an oil into a wax-like substance, such as frequently occurs in cables.

This transformation may also be artificially produced in various ways: (1) in an ozonizer at atmospheric pressure, or still better at a low pressure and high frequency; (2) by an electronic bombardment, using a Coolidge tube, or in a discharge vessel with the oil inside.

**13. Ionization.**—In order to bring about thoroughgoing chemical changes in a liquid dielectric, an adjacent separate air phase must exist besides a high-voltage field. The above-described changes take place at a voltage gradient ranging from about 5 kV/mm up, for then the field strength in the minute air spaces may reach values as high as 12 kV/mm, because of the difference in the dielectric constants; this is sufficient to ionize the air even in very small spaces.

It seems fairly certain from some experiments that an ionization also takes place in pure liquids without air spaces. Only in this case the total energy of impact is not sufficient for producing an appreciable chemical transformation. The occurrence of chemical changes may here be ascertained only by delicate means.

For the theory of ionization we refer the reader to L. Loeb's monograph of this series, entitled *The Nature of a Gas*. Here we shall only briefly discuss the following essential points.

In liquid dielectrics, as in gases, discrete free electrons are always present. How the existence of such free electrons may be explained by external agents, for example, ultra-short penetrating radiations of the atmosphere, has been mentioned in Section 8. The concentration of electrons is, of course, very low. In a field of high intensity these electrons are accelerated and reach finite velocities.

If the field intensity is  $E$ , the force which acts on each electron is  $eE$ , where  $e$  denotes its elementary charge. After an electron has travelled a distance  $l$  in the field it reaches a velocity  $v$  determined by the formula

$$mv^2/2 = eEl \quad (30)$$

Here  $m$  denotes the mass of an electron. The velocity increases as the square root of the free path.

The left-hand side of equation (30) represents the kinetic energy of the electron, and the right-hand side the work done by the field on the electron. The product  $El$  is evidently the voltage over the distance covered. Therefore, the final velocity is proportional to the square root of the voltage covered. In this sense, it is customary to measure electronic velocities in volts. By substituting the numerical values,  $e = 4.77 \times 10^{-10}$  abs and  $m = 9.0 \times 10^{-28}$  gram, the preceding formula becomes

$$v(\text{cm/sec}) = 6.10^7 \sqrt{\text{volts}}$$

For example,  $v = 2.10^8$  cm/sec corresponds to a velocity of about 11 volts.

If the electric field intensity applied to a condenser is known, it is possible to compute the path which must be covered by the electron in order to reach a definite velocity. For example, if the field intensity is 100 kV/cm, a distance of  $10^{-4}$  cm is required to reach the above-mentioned velocity.

In a liquid the molecules are packed so close that the mean free path, that is, the distance which a molecule or an electron covers between two collisions, is very small, of the order of magnitude of  $10^{-8}$  cm. Thus an electron can accumulate only a very small amount of energy at a time, because at every collision it gives up its kinetic energy to the molecule, to be transformed into the heat energy of that molecule.

However, even if the mean path is small, much larger individual paths occur, though rarely. Very short paths and very long paths are possible, the distribution of probabilities of different lengths of path being governed by a sort of Maxwell's distribution curve. Accordingly, paths of  $10^{-4}$  cm, even though few in number, must be considered as existing, and therefore individual velocities may reach values of 10 volts.



Whereas relatively slow electrons can give up their energy at a collision only in the form of heat, very rapid electrons may knock other electrons out of a molecule. Each electron in a molecule is bound to the rest of the structure by electric forces, and in order to remove it from the system it is necessary to apply quite a definite amount of electrical work  $W$ . In accordance with the relationship

$$W = eV \quad (31)$$

a voltage  $V$  may be defined which is usually called the ionization voltage. The order of magnitude of this voltage in gases is 10 volts. In liquids it possibly is much lower, owing to the orientation of dipole molecules around the positive ion produced. If a moving electron has a velocity of  $V$  volts, its energy is just sufficient to release another electron from a molecule. One may picture an impinging electron directly knocking out the other. The kinetic energy of the first electron is then just equal to the potential electrical energy by which the second electron was bound to its molecule. After separation, the velocity of both electrons is nearly zero, and they begin anew their accelerated motion in the field.

Even if we assume an ionization voltage of only 1 volt, the corresponding mean free path at 100 kV/cm is  $10^{-5}$  cm. which occurs very rarely, as mentioned above. But considerations of quantum mechanics lead to the possibility that a moving electron does not lose its energy at each collision by heating the molecule impinged upon. It may accumulate its energy in steps, until the necessary ionization voltage has been reached.

The process of ionization by collision is usually of the nature of an avalanche, and an individual electron which begins its motion from the cathode towards the anode in the course of its path produces many other free electrons. Each newly produced electron loosens more, so that the number of carriers of electricity increases exponentially with the distance from the cathode. It is this rapid

increase in the number of charge carriers that is properly called avalanche-like. We shall now see what the results of such ionization are.

One essential result is a direct increase in the number of conducting particles, which means an increase in the conductivity for direct current. This fact has already been mentioned in Section 8, in connection with the third range of the whole region. (The first range is that of Ohm's law, and the second is a saturation range, if such exists). This rapid increase in the conductivity with increasing field strength often occurs beyond 20 kV/cm, especially with oils containing air, that is, not far from the limit above which saturation has been observed. This circumstance may explain the fact that saturation often escapes observation, being concealed by an opposite and overlapping effect of ionization.

An increase in conductivity as well has not always been observed to the same degree. Some authors have not found such an effect at all, usually because the oil was not sufficiently purified and therefore did not furnish any definite data. At a constant field intensity the phenomenon should be the more pronounced the greater the distance between the electrodes, because an avalanche-like growth of electrons is thereby facilitated. This is actually the case in a carefully performed series of experiments.

Of late, Nikuradse has attempted to obtain quantitative information about the ionization in liquid dielectrics by carefully measuring the currents and the voltages. He has found, for example, that the ionization factor  $\alpha$  (the number of new ions formed by collisions of a single ion per centimeter of its path) obeys the formula

$$\alpha = C(E - E_0)$$

provided that the field intensity  $E$  is not too high. Here  $C$  denotes a coefficient which is a function of the distance between the electrodes.  $E_0$  denotes the lower limit of

field intensity required for ionization. It increases with the degree of purity of a dielectric; with highly purified liquids its values may reach 90 and even 120 kV/cm.

We shall see in the next section that an ionization by collision, which leads first to an increase in the value of conductivity, may finally cause a breakdown of an insulating liquid, provided that the field strength has been sufficiently raised.

A brief discussion of a fundamental question may not be out of place here. As was discovered by M. Wien, an increase in the conductivity at high values of field intensity takes place also in comparatively well-conducting liquids, such as dielectrics with a high dielectric constant, also in water, alcohol, etc. This is due to an entirely different phenomenon and depends upon the so-called Debye effect. Free ions (see Section 8) which are produced by dissociation of an electrolyte exert electrostatic attraction upon each other, and as a result an electrolytic migration of ions is impeded. Therefore in solutions of high conductivity a lower conductivity is usually observed than that computed by equation (13) from the concentration of free ions. As was mentioned above, this effect is mainly observed with a high concentration of ions. These attractive forces of oppositely charged ions cannot be active to the same extent in a high field, on account of greater velocities of the ions, so that the conductivity gradually increases as the obstacles to the motion of ions are removed. For example, the author has investigated this behavior in solutions of picric acid in mixtures of benzene and ethyl alcohol (see Section 8) and has found a very pronounced Wien effect (Fig. 43).

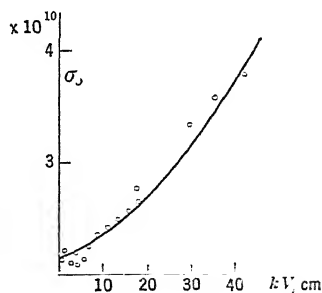


FIG. 43. The Wien Effect in a Semi-conducting Liquid.

It would be of interest to find out whether an increase

in the conductivity of highly insulating liquids, for example, mineral oil, is not due at least in part to a similar phenomenon. This does not seem plausible, because the number of free ions very probably is exceedingly small and not sufficient to produce a Debye effect.

A good criterion for deciding between the two possibilities is the conductivity normal to the direction of an intense field. If ionization by collision is present, the number of free charge carriers is increased, and therefore the conductivity must also increase in a direction perpendicular to that of the applied field. If, however, the Wien effect is the cause of the phenomenon, the initial low value of the transverse conductivity should remain unchanged. The Wien effect is said to be a directed effect.

The author has performed such an experiment with the above-mentioned solution of picric acid and has found the initial value of the conductivity perpendicular to the field unchanged. This shows that at least in this compound a Wien effect took place. A similar experiment for oils has not yet been performed.

The next point to investigate is the behavior of a liquid within this range of ionization by collision, when an alternating voltage is applied. It was mentioned in the introduction to Section 9 that the loss current, according to equation (16), is also sinusoidal. The factor  $\sigma_\omega$  occurs in the equation as a constant, but  $\sigma_\omega$  to a large extent consists of a specific alternating-current component and contains the direct-current conductivity  $\sigma_0$  only as a small fraction.

However, tracing back to the origin of  $\sigma_\omega$ , one finds  $\sigma_0$  also contained therein, at least in the first two groups of losses (see Section 9), which are due to ionic motions.

When the effective value of field intensity is high, the stress varies with each quarter of a cycle from zero to a very high value, or vice versa. During this rise in the field,  $\sigma_0$  must also increase in accordance with the characteristics of conductivity for direct current. Consequently,

$\sigma_\omega$  cannot remain constant either. On the one hand, the specific losses may vary accordingly in a definite manner; on the other hand,  $\sigma_0$  itself may easily rise to the order of magnitude of  $\sigma_\omega$ , so that in this manner the latter also increases with the field strength (Fig. 44). Although the relative change in  $\sigma_\omega$  is considerably less than that in  $\sigma_0$ , yet at high values of field strength it cannot be altogether neglected.

Consequently, in equation (16),  $\sigma_\omega$  is a periodic function of time or of field strength, and  $i_r$  is not a pure sine function by any means. The details of the phenomenon cannot be theoretically described, because  $\sigma_\omega$  as a function of  $E$  is not known to any degree of accuracy. At any rate,

$i_r$  is a much steeper curve near its amplitude than if it were a sine curve. In Fig. 45 a curve for  $i_r$  is plotted, such as has been observed at high field intensities. When a critical field intensity has been exceeded, ionization sets in, and the current rises very rapidly;

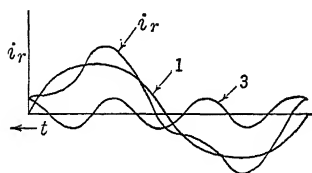


FIG. 45. Distortion in the Curve of Loss Current.

when the field strength drops again, the current decreases accordingly. Using a Fourier series, a periodic curve may be resolved into a fundamental sine wave and the sum of its higher harmonics of different amplitude. The fundamental is represented by curve 1. The hump due to ionization may be represented essentially as a third harmonic, that is, a wave of triple frequency. Curves 3 and 1, added, give  $i_r$ , at least approximately, slight inaccuracies being due to the remaining harmonics, such as the fifth, the seventh, etc., all of small amplitude.

In this manner, when  $i_r$  is known as a function of time,

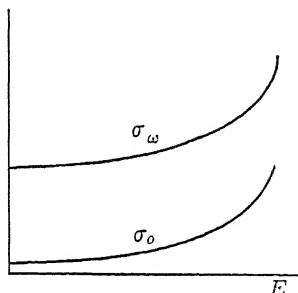


FIG. 44. Conductivity as a Function of the Electric Gradient.

something may be said about the variations of  $\sigma_0$  with the field strength.

Such results may be obtained by an experimental method first indicated by the author. For this purpose a Schering bridge is used, which permits measurement of the loss component of the current. Generally speaking,  $i_r$  is the loss component. When, however,  $i_r$  has been resolved into its harmonics 1, 3, 5, etc. (Fig. 45), then, strictly speaking, only the fundamental is the loss component, because it is only this component that is in phase with the voltage. The higher harmonics do not cause any heat loss. The vibration galvanometer connected in the so-called bridge branch of the Schering bridge (for details see Gemant, *Elektrophysik der Isolierstoffe*, pages 22 and 110) indicates zero current when the bridge is balanced, since the balancing is done with respect to the fundamental wave. However, some higher harmonic currents may still flow in the bridge branch without being indicated on the vibration galvanometer. They may be recorded by means of an oscillograph connected in place of the vibration galvanometer. A simple added arrangement permits either  $i_r$  or the sum of its higher harmonics to be separately recorded oscillographically.

So far no such records have been obtained for pure oil, but only for combinations of oil and paper. These will be discussed in Section 15.

We shall now describe another effect due to ionization by collision, which also may be directly recorded photographically. Those bound electrons which have been released by collisions leave positive ions which gradually drift towards the negative electrode, even though at a considerably lower velocity. Should an electron on its path meet such a positive ion, it may under certain conditions be attracted to it, and a neutral molecule results. The energy of ionization which was stored during the separation as potential energy is now released in the form of luminous energy. Therefore ionization by collision is

usually accompanied by some luminosity, which in gases is well known as corona. Scintillation phenomena in oils have also been known for a considerable time, especially glows about fine wires and sharp points, where the local field intensity acquires very high values. In oils, as in gases, a sudden scintillation of a point under the influence of an impulse voltage may be photographed as a Lichtenberg figure; this has been done, for instance, by Toriyama. (See Section 14.)

Much more definite relationships are obtained in a plate condenser in which the field is of a simpler shape. By making the distance between the plates relatively small, high voltage-gradients may be realized with relatively moderate voltages. When the ionization limit of the liquid between the plates has been exceeded, some luminosity may be expected; the only problem is to show this objectively.

The author has worked out a method of electrophotography for this purpose. A

piece of photosensitive paper which has been sufficiently moistened to become conducting takes the place of one of the plate electrodes. The scintillations are then recorded on the photosensitive emulsion as individual black dots.

The electrocamera shown in Figs. 46 (a) and (b) is suitable for taking such electrophotographs. A metal housing (1) is provided with a high-voltage bushing (2), which must be light-proof. A metal rod (3) may be

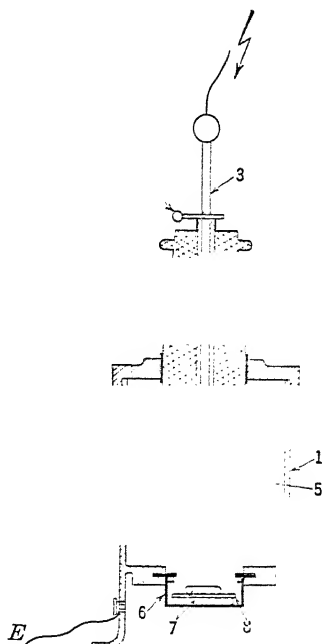


FIG. 46a. A Cross-section of an Electrocamera.

moved up and down in this bushing, being so fitted as to be light-proof; the rod may be fastened in the desired position by means of the catch (4). The upper electrode may be loaded by means of the weight (5). A metal case (6) fits into a guide at the bottom of the housing and is provided with a light-proof cover. Two brass electrodes

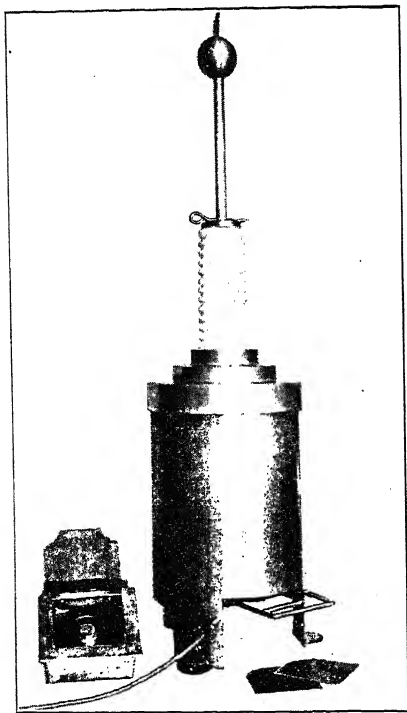


FIG. 46*b*. A General View of the Electro-camera.

(7) are separated by a piece of highly porous filter paper (8). The housing is grounded, and high voltage is brought from the top. The case (6) is assembled in a dark room; it is filled with the liquid to be studied and is provided with a piece of photo-sensitive paper, sensitive side down, between the piece of filter paper and the upper electrode. The case is then closed and pushed under the housing (1), and the cover is removed. The rod (3) is then lowered to make a contact with (7). The filter paper must be thoroughly soaked with the liquid before the

experiment, in order to leave no bubbles of air, which otherwise would give wrong pictures because of intense ionization. It is sufficient to apply an alternating voltage for 20 seconds. After that, the photographic paper is developed.

The records shown in Fig. 47 were made with thin desiccated mineral oil. The filter paper was 0.15 mm thick. The first blackenings (picture *a*) were obtained at



3.5 kV ( $23 \text{ kV}_{\text{eff}}/\text{mm}$ ). This seems to be the lower corona limit. Picture *b* was taken at  $36 \text{ kV}_{\text{eff}}/\text{mm}$ , and the dots are closer together. Picture *c* corresponds to  $40 \text{ kV}_{\text{eff}}/\text{mm}$ . In the last picture, traces of a breakdown are visible, in addition to an intense corona.

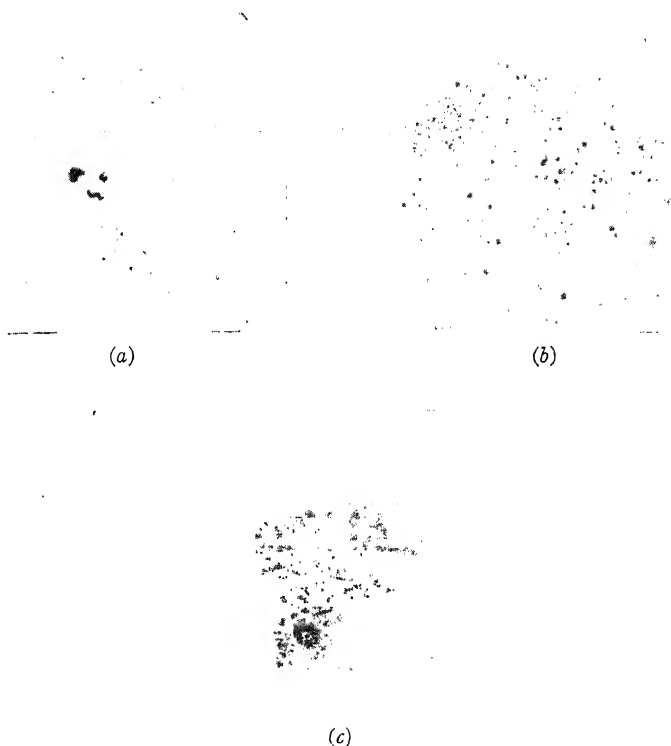


FIG. 47. Some Electrophotographs of Oil.

Such an electrocamera may also be used for an investigation of solid insulating materials. We shall come back to this question in Section 15 when we discuss the combination of oil and paper.

*Summary.*—Electrons endowed with high velocity (which occur in liquids at high field intensities) can split up or ionize molecules and atoms when the ioniza-

tion voltage has been exceeded. New charge carriers are produced by this means, and the conductivity for direct current increases considerably. The loss component of alternating current is thereby distorted, because the conductivity varies with the field intensity, that is, within each half-cycle. The wave contains principally a third harmonic besides the fundamental. The wave form may be obtained by means of an oscillograph connected across a Schering bridge. A recombination of electrons and positive ions takes place with production of light. Beyond the lower corona limit such scintillations take place in a liquid not only at sharp points but also in a uniform field. They may be recorded electrophotographically. A suitable device, the electrocamera, is described, and some actual records taken with oil are shown.

**14. Breakdown.**—When the voltage applied to a dielectric liquid is increased beyond the lower ionization limit, the intensity of ionization phenomena at first increases steadily. Then, at a definite point, the ionization current suddenly increases a great many times in a discontinuous manner. The capacitive current becomes negligibly small compared to it, so that the dielectric in reality becomes a conductor. This phenomenon is known as a breakdown, and the corresponding voltage as the disruptive voltage.

In the last few years this range of voltages has been quite thoroughly investigated, so that the available material is very large. In accordance with the character of this volume we shall mention only the essential points of view and facts; for a more detailed study the reader is referred to the works by Peek and S. Whitehead, and to the author's *Elektrophysik*, mentioned above. An understanding of these phenomena is much helped by the so-called pyroelectric theory of K. W. Wagner and by later contributions by W. Rogowski.

A breakdown is essentially characterized by the fact that the ionization current ceases to represent a steady state. It becomes unstable and grows larger and larger,

and the conductivity seemingly increases without limit. For a long time the cause of instability was not quite clear. Townsend, to whom we are indebted for our knowledge of the fundamental principles of these phenomena, considered the positive ions as the essential factor, especially for gases. So long as only the electrons exert an ionizing action, the current remains stable. As soon, however, as the much heavier positive ions acquire appreciable amounts of energy sufficient to ionize, both ionization currents (positive and negative) tend to increase each other avalanche-like.

Rogowski later proved that positive ions cannot possibly play a decisive part, because if they did, the exceedingly short intervals of time during which a breakdown may be brought about could not be comprehensible. Slepian, and later L. B. Loëb, have pointed out the important rôle of space charges in gases as the principal factor in the understanding of instability. From J. B. Whitehead's investigations we are familiar with the existence of space charges in oils. Therefore there can be hardly any doubt that such charges are as essential in the breakdown of liquids as in that of gases.

The process may be imagined about as follows: The electron current due to ionization increases exponentially from the cathode to the anode. (See the foregoing section.) The principal accumulation of electrons therefore takes place immediately in front of the anode. Of the cations and electrons which are formed here, the latter are quickly swept to the electrode, while the positive ions, because of a considerably lower mobility, due to a greater mass, move away much more slowly from the place of their origin. When the ionization exceeds a certain limit, a positive space charge is formed near the anode, on account of the foregoing reason (Fig. 48). Consequently, the initial straight-line distribution of potential 1 changes into 2, the region to the right of the space charges being practically devoid of electric field. Whereas the initial field strength

was  $U/\overline{KA}$ , (where  $U$  denotes the applied voltage) it is now increased to  $U/\overline{KB}$ . This causes the already intense field of ionization to increase; the space charge grows toward the cathode, the new potential distribution becomes one according to the curve 3, and the new field intensity is  $U/\overline{KC}$ . Finally the space charge extends almost to the cathode, the field intensity becoming very high, equal to  $U/\overline{KD}$ , and the whole space becomes filled with positive carriers, so that the insulating property of the liquid is destroyed. Only the motion of electrons, and not

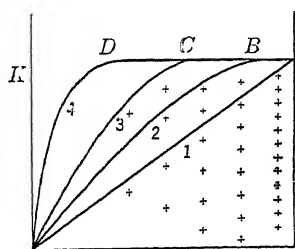


FIG. 48. Building Up of Space Charges before a Breakdown.

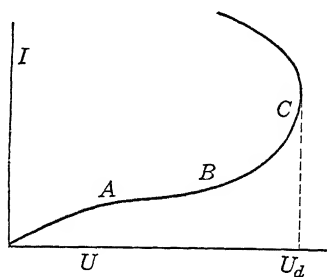


FIG. 49. A Current-voltage Characteristic.

of the sluggish positive ions, contributes to the formation of the space charge in the direction of the curves

$$1 \rightarrow 2 \rightarrow 3 \rightarrow 4;$$

this explains the extremely short interval of time required for the building up of the conditions which lead to a breakdown.

For a formal definition of the disruptive voltage, K. W. Wagner used a current-voltage characteristic, although for an understanding of the details, we must go back to the physical phenomena, as has just been done. A current-voltage characteristic is shown in Fig. 49. In the range up to  $A$  the liquid obeys Ohm's law; from  $A$  to  $B$  is the saturation range, and ionization becomes noticeable beyond  $B$ . When the current  $I$  increases with the voltage

$U$ , the state of the liquid is stable. At  $C$  the effect of the space charge becomes noticeable, so that the current may increase considerably at a constant voltage, in accordance with the four stages shown in Fig. 48. Beyond  $C$  a higher current may exist at a lower voltage, because the resistance of the liquid decreases appreciably. As in the range beyond  $C$  the current increases with a decreasing  $U$ , the circuit is unstable. Each increase in  $I$  causes a drop in  $U$ , that is, an increase in the voltage across the series resistances; this causes  $I$  to increase again, so that an upset of the equilibrium cannot be stopped.

For this reason it is difficult to demonstrate experimentally the unstable range; by using wood electrodes, Wagner succeeded in obtaining such curves on some samples. The point  $C$  evidently corresponds to the breakdown, and the corresponding abscissa,  $U_d$ , is the disruptive voltage. It is impossible to increase the voltage beyond this limit; it represents the highest electrical stress to which the liquid may be subjected.

As soon as the point  $C$  has been reached, the remainder of the curve, in other words, a complete breakdown, is passed over very rapidly. Until recently nothing was known exactly about the interval of time necessary for such a breakdown. It is only in the last few years, since Rogowski has developed his cathode-ray oscillograph for technical purposes, that more definite statements can be made. With this device the quantity to be recorded, for example, the voltage across a liquid, is applied across a small condenser, between whose plates a cathode ray passes in a direction parallel to the plates. At the instant when the voltage breaks down, the initial deflection of the cathode ray is changed without inertia or delay, and the ray describes a streak of voltage variation upon a fluorescent screen or a photographic plate.

The same cathode ray also passes between the plates of another condenser, the plates of the two condensers being in planes perpendicular to each other. At the instant

when a voltage is applied across the liquid, the second condenser becomes charged through a resistance, so that the cathode ray experiences a deflection perpendicular to that due to the first condenser; the velocity of this deflection is known, because the rate at which the condenser is being charged may be computed. This latter deflection takes the place of a time axis, with respect to which the voltage to be measured traces a definite curve.

In this manner the interval of time between the application of a voltage and the breakdown may be quite accurately measured. In liquids and in gases this interval of time is of the order of magnitude of  $10^{-7}$  sec. Thus a stream of electrons actually becomes unstable within a very short time.

For this reason the disruptive voltage is considerably increased when the time of application is reduced to  $10^{-7}$  sec. An increase is noticeable even at somewhat greater intervals, and is called over-voltage. When the interval of time of application of voltage is not sufficient to bring about a normal breakdown, it is necessary to set up an abnormally high ionization in order to accomplish the breakdown. Such experiments are usually made with so-called impulse voltages, which last only a very short time. Such voltages decrease according to an exponential law, and the time constant of the decrease is an approximate measure for the duration of application.

When the time of application is still greater, for instance  $10^{-3}$  sec and beyond, the magnitude of the interval should have no effect upon the breakdown voltage. However, such is not the case. Experiments show that the breakdown voltage decreases with the decreasing frequency of the alternating source. With alternating voltage the duration of a cycle is an approximate measure for the duration of application, because the current and the space charge must be built up anew during each half-cycle. The measured values of disruptive voltage show an effect of the interval of time of application even at  $10^{-3}$  to  $10^{-1}$  sec.

With direct current the disruptive voltage has approximately the same value as the amplitude for alternating voltages of lower frequencies, or perhaps a little lower. All this is an argument in favor of the view that the process of ionization is not the only one which plays a part in this phenomenon. There must be other factors which come into play and lower the value of the disruptive voltage when the time of application is increased.

For still longer periods of voltage application, say over one minute, the dielectric strength also decreases slowly. According to S. Whitehead, the following equation holds true for such intervals of time; this equation was originally deduced by Peek for solid dielectrics:

$$U_d = U_0 + At^{-1/4} \quad (32)$$

where  $A$  is a constant,  $t$  time, and  $U_0$  the disruptive voltage for  $t = \text{infinity}$ . This slow decrease in  $U_d$  is probably caused by a secondary contamination of oil. (See Section 12.)

Before going into the details of the other factors in breakdown, we shall quote a few numerical data:

The disruptive voltage increases with the distance between the electrodes. In the first approximation this increase is linear, so that it is customary to give values of disruptive gradients as a measure for dielectric strength. We shall denote this disruptive gradient by  $E_d$ ; it is of the order of magnitude of 300 kV<sub>eff</sub>/cm. The value of  $E_d$  is not uniquely determined by the chemical constitution of a liquid. This is because it is very difficult to obtain exact numerical data, the results of measurements being quite divergent. According to Hayden and Eddy, such scattering of the data lies in the nature of the phenomena, and with many breakdown tests the measured values are grouped about a mean value in a manner similar to a probability curve.

As mentioned above,  $E_d$  in reality is not constant, because  $U_d$  is not a linear function of the distance.  $E_d$ ,

plotted against the distance  $a$  for abscissas, gives a curve of the shape shown in Fig. 50.  $E_d$  decreases considerably with an increasing distance and is constant, at least approximately, only after the distance has reached a magnitude of at least several millimeters. Therefore it is more natural to take this limiting value as a characteristic quantity. The curve itself may with sufficient accuracy be represented by the equation

$$E_d = E_0 + b/\sqrt{a} \quad (33)$$

where  $b$  is a constant and  $E_0$  denotes the lower limit of dielectric strength.

So far the discussion of the influence of the distance has referred to a plate condenser with a uniform electrostatic

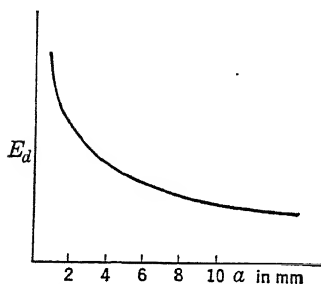


FIG. 50. Dielectric Strength as a Function of Electrode Spacing.

field. In practice one seldom works with plate condensers, and the field is usually non-homogeneous. For instance, one of the electrodes may have a plane surface and the curvature of the other electrode may be varied, keeping the minimum distance between the two constant; in this manner the non-uniformity of the field may be steadily increased. A practical way is to use spheres of smaller and smaller radius for one of the electrodes. The field density is at its maximum immediately at the sphere and gradually decreases toward the plate.

The most natural assumption to make is that a breakdown takes place when the field intensity at the sphere reaches a definite value. This maximum field intensity may be computed if one knows the measured value of the breakdown voltage. Plotting these values of  $E_d$  against the radius of curvature  $r$  of the electrode, it is found that  $E_d$  decreases with increasing  $r$ .

The fact that the critical field intensity increases



when the distance between the electrodes becomes smaller, and also when the non-uniformity of the field becomes more pronounced, agrees with the processes of ionization. It may be shown that a high field intensity alone is not sufficient to bring about a breakdown when the whole available electronic path is too short. The ionization current, which is the decisive factor, is an exponential function of the total length of path, because of its avalanche-like increase. When the path is short the field intensities must be increased accordingly, in order to produce the required current. The conditions are similar near a curved electrode, because there the high field intensity is acting only in the immediate vicinity of the metal surface, so that the ionization path is also very short.

Special conditions appear at the edges of a plane electrode, where the curvature usually is so great that because of the high field intensity a corona glow takes place long before the intensity is sufficient for a breakdown. In the preceding section, in the discussion of ionization phenomena, we have mentioned the phenomenon of luminosity. At sharp edges this luminosity is also known as corona. A lower breakdown is often caused by such a glow; according to Schottky, this is due to over-voltages caused by natural oscillations. Considerable attention should therefore be paid to the shape of the edges of the electrodes.

An extreme case of curved electrode is a metal needle point. At such an electrode an intense corona takes place, owing to the exceedingly high field intensity. If a point electrode be immersed in oil and separated from the opposite electrode by an insulating solid plate, the ionized paths run along the surface of the solid plate in all directions like rays. When a photosensitive plate is used for such an insulating barrier, the whole ionization curve may be recorded photographically. Recording of an electric discharge between a point and a plate was first achieved by Lichtenberg, who discovered such discharge figures in the air. These figures are known as Lichtenberg figures.

More recent investigations, as those of Toriyama, indicate that such Lichtenberg figures also occur under oil.

Positive discharge figures (the point positive) show irregular branched curved paths, whereas negative figures (the point negative) are regular and star-like. There is a fairly reproducible relationship between the radius of the figure and the magnitude of the voltage. A device called a "klydonograph" is based on this principle; it is intended to measure the magnitude of impulse voltages by Lichtenberg figures.

While Lichtenberg figures definitely represent ionization paths, some other facts indicate the presence of other kinds of discharge mechanism. It seems rather certain that a discharge may be produced in a liquid through ionization only in case the liquid possesses quite a high degree of purity. If such be not the case, the liquid will be broken down at a lower voltage, owing to other causes. Most of these factors are much more sluggish than an ionization current; this explains the fact that for relatively long intervals  $E_d$  is a function of time.

As the first among such factors the moisture content of the liquid should be named. When it is sufficiently high a steady conduction current flows through the dielectric. This current may be harmful in different respects, because of the heat which it liberates. First of all, it is conceivable that in some places the local liberation of heat may become so great that portions of the dielectric will be vaporized. Small vapor bubbles are formed which become ionized at comparatively low voltages, just as with air. If such vapor bubbles are present in sufficient quantity, the whole distance between the electrodes becomes ionized, and the breakdown occurs at a much lower voltage than it would in a pure liquid phase. The possibility of such evaporation has been considered by Güntherschulze. Edler has pointed out that evaporation must be accompanied by a time delay; this may explain the probability factor found experimentally by American investigators.

The breakdown is also influenced in a different way by heat liberation. This latter mechanism will be considered in Section 15; it probably occurs but seldom in pure liquid insulators.

Experience shows that the dielectric strength of oil is lowered very considerably when discrete water drops are present. The author has shown that normally spherical drops (Section 2) in an intense electrostatic field become ellipsoidal, so that initially separated spheres may come in contact with each other. A regular aqueous chain may be formed, which naturally allows a very high current to pass through, so that the formation of such a chain is identical with a breakdown.

By means of computations of this kind, experimental curves, which show a rapid reduction in the dielectric strength with increasing water content, may be confirmed theoretically. For example, the dielectric strength of transformer oil with 0.1% water content is only 40 kV/cm; at 0.5% it is 25 kV/cm; whereas well-desiccated oil may show dielectric strength up to 400 kV<sub>eff</sub>/cm.

Besides water content, the air content of a liquid should be mentioned (Section 5). Since the dielectric strength of air is roughly one-tenth that of a liquid dielectric, it is clear that an appreciable air content must be harmful. It has been actually observed that an evacuation of an oil considerably increases its dielectric strength. Moreover, not only the air content of the liquid itself but also that of the electrodes must be taken into consideration. A thorough degassing of the electrodes also increases the values of breakdown voltage.

It may be asked how air reduces the dielectric strength. The author explains this fact by assuming that at first a small air bubble is formed near one of the electrodes, which bubble is then lengthened by electrostatic forces, owing to an ionization within. After the elongation has reached a certain limit the bubble becomes unstable and continues to stretch in the direction of the field like a

thread, until an air bridge is formed between the electrodes. A breakdown then takes place along the whole path. In the first approximation

$$E_d = \sqrt{\gamma/r}(\text{kV/cm}) \quad (34)$$

where  $\gamma$  denotes the surface tension of the liquid and  $r$  the radius of the initial air bubble. Since  $\gamma$  is approximately equal to 30 dynes per cm and  $r$  is of the order of magnitude of  $10^{-3}$  cm,  $E_d$  must be of the order of 200 kV/cm.

The foregoing considerations show the importance of freeing insulating liquids as far as possible from moisture and air; this subject is treated in Section 5.

*Summary.*—In a pure liquid dielectric a breakdown takes place because the ionization current becomes unstable. The current increases steadily as the voltage drops. This instability of the current may be explained by the presence of positive space charges. A complete breakdown takes place within  $10^{-7}$  sec, this value having been ascertained by means of a cathode-ray oscillograph. That the disruptive voltage is a function of time even at greater time intervals proves the existence of other, more sluggish factors in a breakdown, such as may act in a dielectric which contains moisture and air bubbles. The disruptive field intensity,  $E_d$ , increases considerably with the decreasing distance between the electrodes and the decreasing radius of their curvature. Characteristic discharge figures which originate at a point electrode not only may be observed in air but are typical for oil as well.

## CHAPTER VI

### APPLICATIONS TO ELECTRICAL ENGINEERING

**15. High-Voltage Cables.**—It is in the high-tension cable, above all other forms of apparatus, that the liquid dielectric of electrical engineering, mineral oil, is subjected to the most intense continuous stress. Such cables serve for the transmission of large amounts of electrical energy, transformed to a high voltage in order to lower conductor losses. With a given amount of power, the current  $I$  becomes correspondingly lower, and so does the voltage drop  $IR$  in the resistance  $R$  of the conductor.

Overhead transmission lines are used in the open country between large centers of population. In the vicinity of large cities, overhead conductors are often inadmissible, and electric energy must be transmitted underground, by means of cables.

Such a cable consists of an inner metal conductor subjected to a high voltage; to reduce the resistance this conductor is made of copper, which is surrounded with some insulating material; a lead sheath, usually kept at ground potential, is provided on the outside. Lead is used, rather than some other metal, in order to preserve the required flexibility of a cable. A steel armor is sometimes provided outside the lead sheath for the mechanical protection of the cable.

The insulation consists of wound layers of paper tape, impregnated with oil, which fill the space between the central conductor and the lead sheath. For this purpose unsized paper is used, the so-called cable paper, which consists only of cellulose fibers. By rolling or calendering

at different pressures such paper may be given different degrees of porosity as desired. The average "fill factor," the ratio of the volume of the cellulose to the total volume, is about 0.4 for uncalendered paper and 0.6 for calendered paper.

The paper is wound as tightly as possible, so as to fill up practically the whole available volume. In spite of this, small air pockets remain between the individual layers of paper. Empty spaces are also unavoidable at the overlaps of the edges of the paper tape, and as mentioned above, there are pores within the paper itself. For first-class insulation the air must be removed from all the spaces as far as possible, and for this reason the process of impregnation constitutes the most important operation in cable manufacture.

It is theoretically impossible to remove all the air. Microscopic amounts of air are unavoidable. Assuming the larger pockets to be filled with oil and even the pores within the paper impregnated with oil, there still remain individual cellulose fibers, which may be thought of as a system of separate crystallites between which amicronic air gaps will still be present. Oil does not penetrate into these air spaces. If it did there would be a swelling of fibers in oil, accompanied by a visible thickening of the fibers. For example, fibers do swell in water, but not in a mineral oil. This means that the crystalline structure of the fibers is not at all affected by the oil. In some respects this is of advantage, because a swelling of the fiber structure would be accompanied by its loosening. A piece of paper soaked in water tears very easily, whereas a piece dipped in oil has as much resistance to tearing as a dry piece. On the other hand, a disadvantage is that air, when present in such small quantities, cannot be crowded out by oil.

For this reason a cable insulation is to be considered as a three-phase system, consisting of oil, paper, and air. This fact justifies a separate treatment of this system. Otherwise we could simply refer to the preceding sections

in every respect. Because of this triple combination, additional properties become manifest, which we shall now discuss in detail.

First a few words should be said in regard to the process of impregnation. The principal steps are as follows: After the paper tape has been wound on the conductor, the cable is first dried in order to remove most of the moisture; then it is subjected to a vacuum in order to remove the air. While it is still in vacuum, oil is admitted. This oil has previously been treated by heat and vacuum. The whole system is then subjected to a vacuum for some time before atmospheric pressure is again admitted.

The necessary conditions for the success of this process are, first, a sufficiently high wetting tension of the oil with respect to the paper (Section 2), in order to fill the pores thoroughly, and secondly a proportionately low viscosity of the oil (Section 3), to allow a sufficiently rapid movement of the oil within the paper capillaries. The first condition is probably always fulfilled. It is believed that the addition of rosin, which is an acid-like substance, increases the wetting of the paper. Since impregnation always takes place at a high temperature ( $110^{\circ}\text{C}$ ) the viscosity of even a heavy oil is sufficiently low. The addition of rosin to an oil further reduces the viscosity at high temperatures. Rosin in this way acts favorably throughout the process of impregnation, and for this reason mixtures of oil and rosin, so-called impregnating compounds, have been quite popular. Of late, however, for other reasons (see further below), lighter mineral oils, such as transformer oils, have been used in place of impregnating compounds.

With the use of an impregnating compound which later solidifies when cooled, a finished cable can be taken out of the tank and run through a lead press. Thus from the standpoint of manufacture, the hardening of the compound is an advantage. However, this kind of impregnation is not very thorough or favorable, because the layers adjacent to the inner conductor, which are subjected to the highest

field intensity, are those most remote from the oil in the impregnating tank. Air pockets may therefore be expected to remain in just these portions of the insulation. A change from a heavy insulating compound to a lighter oil in itself means a change in the process of manufacture, because a cable could not be lifted out of the tank without the possibility of losing some oil.

A different process has therefore been developed, which at the same time removes the objection of having the inner layers of paper poorly impregnated. A cable is leaded while dry and then impregnated with oil from the inside instead of outside. The conductor is hollow and allows a free passage of the oil between the individual copper strands of its cylindrical body. The cable is filled with oil and impregnated from inside, under vacuum. The most unfavorable places are now immediately under the lead sheath; with reference to the electric field these places are the least dangerous. The essentials of this process were originated in the Italian Pirelli Works.

We shall now consider separately the individual properties of a finished cable.

For the direct-current conductivity the statements in Section 8 hold true, with the following essential limitation. The conductivity of the oil is considerably reduced by the presence of the paper. This fact has been brought out by Emanuelli in particular, and the author has performed some measurements which confirm it. Even at low field intensities (100 to 1000 V/cm) the conductivity of an oil in the presence of even slightly calendered paper is reduced in the ratio of 130 to 1. The same ratio is obtained by using, instead of oil, dekaline, which is a volatile hydrocarbon. This phenomenon has not yet been followed more closely. It cannot be explained by a simple reduction in cross-section, because the "fill factor" of paper is about 0.5. Either the mobility of the ions is much impeded by the narrowness of the pores, or else the concentration of free ions is very much reduced because of adsorption on the fibers.



The dielectric losses are affected in the opposite direction. Whereas at ordinary frequencies they are very low in oil (see Section 9) and are mainly caused by space charges, the losses in a cable are larger. The reason is that because of a layer structure a typical Wagner effect may take place. The conductivity of cellulose fibers by themselves is certainly different from that of the oil (it is smaller when they are absolutely dry, and higher with traces of water), so that  $k$  in Equation (20a) is different from zero. In cables the value of  $\tan \delta$  has been found to be of the order of magnitude of 0.005.

The relationship between  $\tan \delta$  and the applied field intensity is worthy of notice. Usually there is a small increase with the voltage, as is mentioned in Section 9. If, however, more air is left than is desirable, the air bubbles become ionized at a relatively low field intensity, and  $\tan \delta$  increases rather rapidly from this point on. The curve between  $\tan \delta$  and  $U$  is known as the loss curve, and the point of a sudden rapid increase is called the ionization point. It indicates that the cable contains too much air.

Dawes endeavored to determine variations of  $\tan \delta$  with  $U$  on glass models, partly by computation and partly experimentally. The author has carried out more rigorous computations. The results indicate a steep rise in the curve, a maximum often observed at higher voltages, and a subsequent drop of  $\tan \delta$  with the voltage. The computations are based on the assumption that the losses are due to periodically recurring individual breakdowns of the air gaps. The number of such breakdowns per cycle increases with the voltage; this was proved oscillographically by the author and Philippoff, using a model arrangement consisting of a condenser in series with a spark gap. Conversely, on the basis of such computations, the number and the magnitude of air pockets in a cable may be determined from a given loss curve. The order of magnitude of the percentage of the air volume is the same as that of the maximum change in the loss angle.

The dielectric constant  $\epsilon$  of a finished insulation is

higher than that of pure oil. On the average it is 3.5, as against 2.3 for pure oil. This is because the dielectric constant of paper alone is about 6. The higher the "fill factor" of the paper, the higher is  $\epsilon$  for the finished cable. Occasionally a tougher paper is used for the inner layers, in order to have here a higher value of  $\epsilon$ , and in this way somewhat to equalize the non-uniform distribution of the electric field.

Of great importance are the *motions in oil* which are not due directly to the field, but are caused by temperature rise (Section 11). When a heavy current flows through the conductor the temperature of the cable rises up to 80° C. Although the heat produced is being steadily conducted to the outside (Section 4), yet in a steady state of the cable the temperature of the oil becomes quite high. An expansion of the oil causes the lead sheath to stretch, so as to provide sufficient space for oil. During the following rest period, when no current is flowing through the cable, the impregnating compound is again contracted, whereas the lead retains its form; as a result, empty spaces are formed within the insulation. Such pockets become filled with gases and vapors and constitute a troublesome feature of the insulation. Such a motion of the oil is called "breathing." Naturally efforts are made to reduce it as much as possible.

A particularly undesirable feature of this phenomenon, resulting from frequent changes in the temperature, is that empty spaces are formed mainly in the inner layers of the insulation, as has often been observed. The inner layers begin to look dry, as though the mass of the oil had gradually drifted outward. Because of this, the cable deteriorates considerably, for its quality essentially depends upon the proper functioning of the inner layers of the insulation.

To prevent these undesirable changes, the use of a lighter oil in place of a heavy impregnating compound has been recommended. The principal reason for the formation of empty spaces is that the impregnating compound

becomes so viscous when it cools down that it cannot flow back rapidly enough, and thus causes the formation of the pockets. When an oil remains fluid even at low temperatures, as does transformer oil, and when provision is made for replenishing it, say out of a hollow conductor, the whole insulating space remains filled with oil when the cable is cooling down, and air pockets cannot form at all.

With this system the hollow inner conductor is put in communication with so-called equalization tanks. These are oil reservoirs placed at distances of about 2 km from one another and connected with the hollow conductor. In these tanks the oil is under pressure, so that when the cable is cooling down, the oil is being forced into it, whereas during the periods of temperature rise in a cable these tanks provide place for an expansion of the oil. Usually a pressure of a few atmospheres is provided by means of nitrogen gas.

This solution of the problem is not perfect, because nitrogen becomes gradually diffused in the oil and in time may become liberated within the insulation. According to Pirelli's later procedure, the oil reservoirs are completely filled with oil and contain no gas phase. Special closed hollow metallic bodies are mounted either in each reservoir or inside the hollow conductor; these bodies change their volume elastically in accordance with the outside pressure. This gives an opportunity for the oil to expand; it is forced back between the layers of paper when the cable is cooling down. Such a cable system is somewhat complicated, but operates in quite a satisfactory manner.

Another proposal, that of Felten and Guillaume, consists in placing a cable under external pressure upon its whole length, in order to resist the "breathing" which leads to the formation of pockets.

The essential reasons for the formation of wax under the influence of an electrostatic field have been explained in Section 12. Its formation is facilitated by pockets due to the "breathing" of the cable. The above-described

protective measures actually bring about a great reduction in wax formation.

The following may be said in regard to ionization in cables: Since the insulation consists of oil, paper, and residual air, the total ionization may be thought of as the sum of ionization in the air and in the oil. A direct separation of the two components is not easy, and it is of

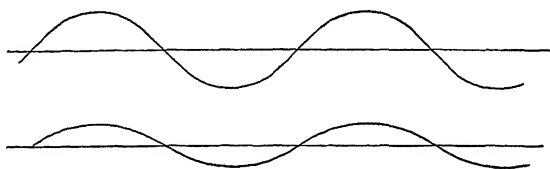


FIG. 51. Cable Oscillogram at 23 kV/cm.

importance to know when the first traces of ionization become noticeable. If the limit is low, say about 30 kV/cm, then the cable contains air; if this limit is considerably higher (say 100 kV/cm), then it is the oil itself that becomes ionized.

The first traces of ionization are best measured with alternating voltage. Oscillograms such as have been

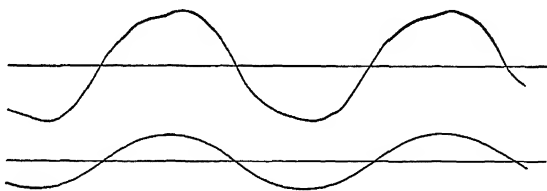


FIG. 52. Cable Oscillogram at 30 kV/cm.

described in Section 13 are very useful. The following records have been obtained on a high-voltage cable of smaller type, impregnated with a compound; the insulation was 4 mm thick. Fig. 51 was taken at 23 kV/cm, and Fig. 52 at 30 kV/cm. The lower curve is the voltage, and the upper curve the total loss current. While in Fig. 51 the latter is a pure sine wave in phase with the voltage, an appreciable distortion is visible in Fig. 52.

This is the first indication of an existing ionization. Since the field intensity is quite low, the ionization must have been caused by air bubbles.

Fig. 53 is a record at 43 kV/cm; the distortion is quite considerable. The higher harmonics were taken at the same time; it will be seen that they consisted mainly of the third harmonic. An ionization of the oil itself should occur at a considerably higher value of voltage gradient.

Simultaneous measurements of the loss angle as a function of the field intensity gave an ionization point at 25 kV/cm.

Such small amounts of ionization as those shown in the above oscillograms are not nearly so harmful as has often been assumed; Whitehead has recently called atten-

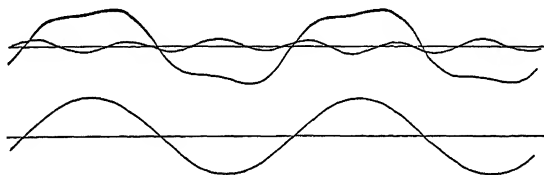


FIG. 53. Cable Oscillogram at 43 kV/cm.

tion to this fact. (See further below.) It is therefore desirable to have a method of measurement which is not so sensitive as the measurement of the loss angle. Such a method may be found in the process of electrophotography described in Section 13. This method indicates the voltage gradient at which an initial visible corona takes place. Luminosity appears first at a higher field intensity than the first traces of ionization, which correspond to a dark discharge. Thus a determination of the corona limit furnishes the value of the voltage beginning with which a definite destruction of the cable may be expected.

We have previously given the lower glow limit of oil alone as 230 kV<sub>eff</sub>/cm. When oil exists only in paper pores, however, the formation of appreciable ionization currents

is made much more difficult, and this limit lies higher. According to the author's measurements, it is somewhere near  $400 \text{ kV}_{\text{eff}}/\text{cm}$ . Below such high stresses (which do not occur in a cable) any ionization that may take place will give rise to a corona. If the corona threshold is below the values given above, it is surely harmful for the cable. A test of this sort should therefore be considered as decisive for the quality of impregnation.

With one layer of strongly calendered paper, saturated with oil at  $110^\circ \text{C}$  in high vacuum, the relationship between the time of impregnation and the corona threshold, measured electrophotographically, was found to be as shown in the following table:

Time of impregnation	Corona threshold in $\text{kV}_{\text{eff}}/\text{cm}$
1 minute	180
3 minutes	230
10 "	300
30 "	300
1.5 hours	300
4 "	350
12 "	410
36 "	410

Fig. 54 shows electrophotographs after 10 minutes of impregnation at 300 and 400  $\text{kV}/\text{cm}$ , and Fig. 55 shows them after 12 hours of impregnation at 400 and 550  $\text{kV}/\text{cm}$ . In Fig. 54 the corona threshold is 300  $\text{kV}/\text{cm}$ , and in Fig. 55 it is 400  $\text{kV}/\text{cm}$ .

It will be seen that impregnation becomes complete and practically free of air only after about 12 hours. Beyond this time the corona limit cannot be raised any more. An ionization point in the curve may perhaps occur even after 12 hours of impregnation, but it will be without practical significance. Strictly speaking, the results of the foregoing experiment hold true only for one layer of

paper; for several layers the intervals of impregnation should be correspondingly higher.

What are the facts about breakdown in high-voltage

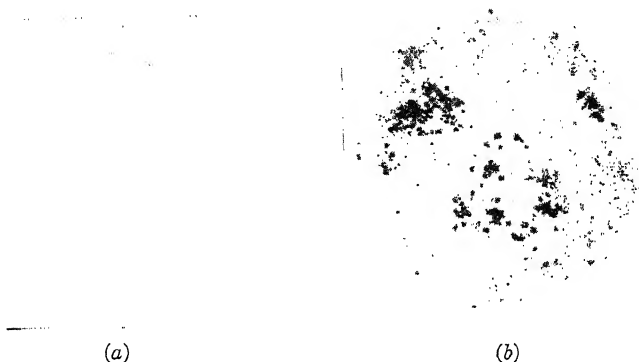


FIG. 54. Electrophotographs of a Cable Insulation; Impregnation Time, 10 min, (a) at 300 kV/cm, (b) at 400 kV/cm.

cables? The discussion in Section 14 must be somewhat modified. Substantially, the presence of paper causes an increase in the dielectric strength. Whereas for oil alone



FIG. 55. Electrophotographs of a Cable Insulation; Impregnation Time, 12 Hours, (a) at 400 kV/cm, (b) at 550 kV/cm.

it lies between 300 and 400  $\text{kV}_{\text{eff}}/\text{cm}$ , measurements on finished insulation give values of 500 to 600  $\text{kV}_{\text{eff}}/\text{cm}$ . The reason for this increase in dielectric strength lies possibly

in the difficulty with which ionic currents can be formed, because of a reduced cross-section in the pores. This conclusion could also be derived from electrophotographic records, which show a distinct increase in the limiting corona voltage.

Since the dielectric losses are higher in a cable than in oil alone, an increased amount of heat generation must be expected. The pyroelectric mechanism of breakdown, discovered by K. W. Wagner, should often be the determining factor in cables. Such a breakdown is based on the fact that the conductivity increases exponentially with the temperature (Section 8). If there is a spot in the insulation at which the losses are slightly higher than in the surrounding mass, the development of heat and to some extent the temperature rise are concentrated at this spot. The electric conductivity increases, and with it the temperature, so that a state may be reached at which a stable equilibrium is no longer possible, and the current will increase without limit. This is equivalent to an ultimate breakdown.

When the load is continuous, such local accumulations of heat should be watched with particular care. In heavily loaded cables hot spots have quite often been found, and it is known that they are the places most subject to breakdown.

A cable can stand a somewhat higher direct voltage than alternating voltage, especially if the effective values are compared. In the first place, the ionization is much weaker, because with direct voltage the conductivity of layers of air in series with oil cannot exceed the conductivity of the oil itself; in the second place, the heat losses are considerably lower than with alternating voltage, so that a pyroelectric breakdown becomes improbable. For these reasons cables lend themselves particularly well to power transmission at extremely high direct voltages.

In conclusion a few words should be said about the testing of cables. It is extremely desirable to have a



method which within a short time will give information about the probable actual life of a cable under operating conditions. Much in this direction has been accomplished by the recent researches of J. B. Whitehead and F. Hamburger. According to them, the usual standards of testing, for example, the shape of the curve of  $\tan \delta$ , are by no means sufficient. A flat curve for  $\tan \delta$  is no more a convincing promise of a long life for the cable than a rising curve is a proof of a defective cable.

It may be said that the curve for  $\tan \delta$  shows whether or not air pockets have been left in the cable, and to what extent they remain. But air pockets are only one of the many fundamental defects which a cable may have. Therefore such a test does not furnish a final indication about the quality of the cable.

The degree of vacuum to which the cable was subjected during the impregnation should also be considered a factor in any judgment about its quality. According to Whitehead, however, this too should not be taken without limitations. Impregnation pressures of over 25 mm of mercury are of course bad and should not be permitted. However, a reduction in the pressure below the foregoing value does not necessarily bring with it a longer life for the cable. The impregnation of course will be more thorough, but this in itself is not a decisive factor.

Besides the thoroughness of impregnation, certain rather indefinable properties of the oil and the paper are of importance. A simple test for the general quality of these materials has not yet been developed.

One is therefore compelled to apply direct tests of short duration in order to obtain an approximate idea about the useful life of a cable. Whitehead recommends the following tests:

160 kV/cm during 22 hours  
200 kV/cm during 22 hours  
240 kV/cm during 112 hours  
280 kV/cm until breakdown

Loss measurements at 4-hour intervals are recommended. The total life of the sample, determined by means of this short test, furnishes a reliable basis for judgment about the general quality of the cable.

During the first few hours of such a test the value of  $\tan \delta$  always increases in steps. This initial increase in  $\tan \delta$  has been found to be approximately inversely proportional to the life of a sample. This gives a purely empirical and by no means final indication of the life to be expected in actual operation.

With the aid of such a test, Whitehead recently showed that oils of low viscosity (high penetrating power), in particular those of a naphthenic base, are the most favorable for the life of a cable.

*Summary.*—Cable insulation is a three-phase system consisting of oil, paper, and residual air. The properties of pure oil are modified accordingly. After a brief description of the process of impregnation according to two different principles, the individual properties of cable insulation are discussed. The presence of paper reduces the direct-current conductivity of the oil, but increases the dielectric losses and the dielectric constant. With increasing voltages the losses often reach a maximum and decrease again. Liberation of heat within the cable causes the so-called breathing, which easily leads to the formation of pockets. These drawbacks have been remedied in the new "pressure" (oil-filled) cable. Ionization in air pockets leads to formation of wax. The beginning and the degree of ionization are measured by the shape of the loss curve. Some information about ionization processes may be obtained from oscillograms and also from electrophotographs. The disruptive strength of the composite insulation is higher than that of oil alone. A pyroelectric breakdown often takes place. For judging the quality of a cable, life-tests of short duration may be used. Whitehead's investigations on this subject are briefly described.

**16. Transformers.**—In a high-voltage transformer the oil serves a twofold purpose. It helps to insulate the winding, and it conducts away the heat liberated by the current and by the iron core.

So far as its first function is concerned, the stresses are not nearly so high as in a cable, because the voltage between the adjacent windings is always limited. Of course, transformers are often subjected to travelling waves, which mainly exert their harmful influence upon the end-turns. The potential difference between the adjacent turns is then very much increased. It is sufficient to refer the reader to the principal statements in Section 14. Moisture is of particular importance, because of the difficulty of keeping it out of an oil for any length of time. A certain amount of water is always present in transformer oil. So far as the electric stresses are concerned, portions of the coils with a relatively small radius of curvature must be closely watched, because considerable local stresses may be produced at such places. It may be of interest to mention that in this respect moisture may be favorable, because it covers the wires and thus reduces their curvature.

For the function of oil as conductor of heat, reference is made to Section 4. It is there shown that the ability to remove heat depends primarily upon the diffusivity and the specific heat of the material. However, the phenomenon is not fully determined by these. A cable, on account of its solid structure, may be approximately treated as a simple solid conductor of heat. On the other hand, in a transformer the oil may circulate freely, so that convection plays an important part. The oil in the immediate vicinity of a winding is strongly heated; it rises, owing to expansion, and gives up its heat to the tank by conduction. The important factors are the expansion coefficient of the oil and its viscosity, because the latter essentially determines the velocity of circulation (Section 3). With these in view, the oil must be as light as possible. Moist surrounding air is also favorable. It is known that the

cooling action of the air is increased by humidity. For example, with normal humidity (33%) and at an air temperature of 30° C, 25% less air is sufficient for the same cooling action which dry air would have.

In this connection the solidification point of the oil is very important, because at this point the circulation practically stops. Paraffin oils are particularly unfavorable in this respect, because they have rather definite points of solidification, often in the vicinity of 0° C, and then form a network-like structure. The cyclic naphthene oils are decidedly better, because they solidify at lower temperatures and only gradually, the freezing point not being so pronounced.

If a transformer is switched in when the oil is at a temperature below the solidification point, the windings at first become exceedingly hot. It is only after the ambient oil has been warmed up to its melting point that an intense cooling action begins, and the temperature of the windings drops. Some tests at the Brown-Boveri Works in Switzerland have shown that the windings do not become overheated beyond the permissible temperature limit (90° C) so long as the point of solidification of a paraffin oil is not higher than about 4° C. It is wise to be guided by this figure unless a naphthene oil is used.

We shall now discuss in more detail the oxidation of oil in actual operation. The following may be added to the general view given in Section 7.

An oil is modified by a continued high temperature, and this leads mainly to two harmful results. In the first place, a compound is formed within the oil which attacks the cotton covering, so that the insulation of the winding becomes steadily worse. Secondly, a solid product is formed, so-called sludge, which to some extent sticks to the winding and impedes a free circulation of the oil.

Fundamentally, the chemical reaction which lowers the quality of the oil is its gradual oxidation. Acids are

formed, partly volatile and partly asphaltogene acids of high molecular weight. A combination of two acid molecules, with a liberation of a water molecule in both  $\text{COOH}$ -groups, leads to a formation of anhydrides, in this particular case of the asphaltenes. These are neutral substances which, together with the naphthenes, form the above-mentioned sludge.

The oxidation does not proceed directly, but through the intermediary of catalysts, which first absorb oxygen to form peroxides, and then give up half of the oxygen to the oil. The S-shape of the curve which gives the amount of product of the reaction as a function of time proves among other things that the process is of the so-called auto-catalytic type. The velocity of the reaction is at first low, then becomes high, and slows down again with the lapse of time. The peroxides which are formed as intermediate products are mainly responsible for the destruction of cotton fibers. They oxidize cellulose in the same way that they oxidize oil.

In addition to this harmful effect, an oxidation of oil leads to some other consequences. It follows from the foregoing reactions that the amount of acids in the oil is increased. The so-called acid number, that is, the analytical measure for the acidity, becomes higher. As a result, the electric conductivity increases, and the disruptive strength decreases. Moreover, the viscosity is increased, since the anhydrides remain in the oil, even though partially in a colloidal state. This is unfavorable for the free circulation of the oil. Finally, the boundary tension of oil against water is also modified. On the basis of the latter modification Nuttall has proposed a method for testing the permanency of an oil.

In the first place, among the external factors which affect oxidation the temperature should be mentioned. In particular, the existence of a critical temperature in the vicinity of  $120^{\circ}\text{C}$  has been found; above this temperature the chemical reactions become quite different, and the

deterioration of the oil proceeds at an especially high rate.\* Of interest are the tests which definitely prove an accelerating action of light, indicating that some photochemical factors must also be acting. However, H. Stäger, who has been one of the most active workers in this field, has shown that light exerts an influence only when air comes in contact with oil at the same time.

Quite a number of catalysts are known which accelerate oxidation (see Section 7). In the first rank must be mentioned metals, such as copper, brass, and iron. Lead occupies a separate position; it does not cause formation of sludge, because it combines into lead salts with the acids produced. Occasionally these salts become precipitated in the form of flakes.

There are also negative catalysts, so-called antioxidants or inhibitors, which retard oxidation. As such may be named phenyl- $\alpha$ -naphthylamin, diphenylhydrazin, sulfur, nitrobenzene, etc. Nothing definite is yet known about the mechanism of the action of such substances. Inhibitors have been investigated in detail by Brian Mead.

It is also known that the addition of an inferior oil to a good one, even in a small quantity, considerably increases the oxidation. This is the reason for the rule that when new oil is added to a transformer it should be as nearly as possible of the same quality.

The question arises as to the most effective way of combating oxidation. For this purpose the so-called refining of oil is employed, which consists in subjecting it to certain processes to make it more stable. The most important agent used is sulfuric acid, which oxidizes admixtures that are easily oxidizable and thereby removes them from the oil before use. By testing an oil for acid content and sludge formation as a function of duration of refining, both will

\* The general validity of this as a critical temperature in all oxidation seems questionable, in the light of a large amount of work done in some American laboratories. Differences in the types of oil investigated may be responsible for the discrepancies.—Translator's Note.

be found to decrease with time. However, whereas the formation of sludge remains low, the curve of acid formation passes through a minimum. An oil which has been refined too far, a so-called over-refined oil, is more apt to form acids. Therefore over-refining should be avoided.

Stäger has found that in this respect naphthene oils are superior to paraffin oils, because the former show a quite flat minimum, whereas in paraffin oils the minimum is rather sharp. For this reason the use of naphthene oils is recommended. In any case the process of refining must not be carried so far that acid formation again becomes greater.

The objection to over-refining is that it leads to so-called cracking. Sulfuric acid not only attacks easily oxidizable components, but also finally splits some heavy molecules into lighter ones. If this secondary process is allowed to go too far, too many smaller molecules come into being and later form acids quite readily. Since they are not easily polymerized, sludge formation remains low, and only the acid number increases.

*Summary.*—The function of the oil in a transformer is to insulate the windings and to conduct away liberated heat. The essential properties of oils for these purposes are briefly described. Operation at a fairly high temperature for a considerable time causes an oil to oxidize easily. Acids and sludge are formed. The insulation of the windings is thereby affected, and free circulation of oil is impeded. The various factors which affect the velocity of oxidation are discussed. There are positive as well as negative catalysts. The oil should be previously treated with sulfuric acid, that is, refined; however, over-refining should be avoided.

**17. High-Voltage Circuit-Breakers.**—A third application of dielectric liquids is found in high-voltage circuit-breakers. Owing to the enormous amounts of electric power to be interrupted (voltages of the order of 100 kV and simultaneously currents up to 10,000 amp), an electric

arc is produced when the contacts are separated. At the moment of origin it is simply a break spark, but a high current heats the electrodes to such a degree that they begin to emit electrons spontaneously. Whereas a spark produces its own carriers of electric charges by ionization by collision, a different form of discharge, called an arc, is produced with hot electrodes and high intensities of electron emission. An essential characteristic of the arc is its high temperature, which reaches  $3000^{\circ}$ , or according to more recent investigations, even up to  $5000^{\circ}$  C.

If the arc should persist for an appreciable interval of time, the contacts would be completely destroyed. Therefore the principal function of a circuit-breaker is the rapid extinguishing of the arc. This end is partly accomplished by having the contacts immersed in oil. First, the oil causes an intense cooling of the electrodes, and secondly, it contributes directly to extinguishing the arc. A high velocity of charge carriers, such as is necessary to maintain a current, can exist only in a gas phase. In an oil the mean free path is too short, so that a current is promptly interrupted. As a result, an arc is extinguished within a fraction of a second, or with alternating currents, after a few half-cycles. On account of the natural periodic passage of an alternating current through zero, an alternating arc can be extinguished more readily than a direct-current arc.

Both functions are best performed by a mineral oil. One of the principal difficulties is at low temperatures, when the oil becomes thick and cannot flow freely toward the electrodes. This circumstance has already been mentioned with transformers; here it is even more important. At the instant of formation of an arc a space filled with vapor is formed, and if the solidified oil cannot flow into this space rapidly enough the arc hangs on.

In this application, naphthene oils, because they become solid gradually, are preferable to paraffin oils. It is of the greatest importance to determine the point of



solidification of the oil to be used. It is not sufficient to determine only one point; it is best to take the whole viscosity curve, as explained in Section 3. With a paraffin oil the curve is not single-valued, and the viscosity is different at rising and falling temperatures (hysteresis). The reason is that when the temperature decreases some insoluble constituents often remain, in the form of the so-called supercooled solution, before a colloidal precipitation begins (Section 6). Consequently, the viscosity curve remains rather low. It is only after all the insoluble constituents have been precipitated that the viscosity increases quite considerably; since unstable solutions do not exist with rising temperature, the whole curve lies higher. It is therefore preferable to work with the rising branch of the curve, because the conditions so obtained are more nearly those of a state of equilibrium.

Another difficulty in the operation of oil circuit-breakers is decomposition of the oil, due to repeated interruptions of the circuit. In a transformer the oil usually is maintained steadily within a temperature range between  $60^{\circ}$  and  $80^{\circ}$  C, but in an oil switch it is brought up for short periods of time to  $3000^{\circ}$  to  $5000^{\circ}$  C. The results of elevation to such high temperatures for even a short time are quite radical. Some of the oil becomes completely decomposed. Solid, liquid, and gaseous decomposition products are formed. The solid products, the so-called circuit-breaker sludge, consist primarily of carbon, although also partly of hydrocarbons. The liquid products are of low molecular weight; this is proved by the fact that after the repeated breaking of the circuit the ignition point of the oil becomes lower, and also that when analysis by boiling is made, the percentages of substances which become distilled under  $300^{\circ}$  C increase rapidly. However, these liquid products are relatively unimportant. It is the gaseous products that are of the greatest significance. They consist of about two-thirds hydrogen gas, a quarter of hydrocarbons, and the remainder carbon dioxide, oxygen,

and nitrogen. The best known among the hydrocarbons are methane  $\text{CH}_4$ , ethylene  $\text{C}_2\text{H}_4$ , and acetylene  $\text{C}_2\text{H}_2$ .

From a certain point of view the influence of gaseous products is favorable. Since they cannot escape rapidly enough out of the explosion chamber, their pressure increases considerably, and in this way they help to interrupt the current. This property of oil gases is utilized in a type of circuit-breaker in which a completely closed pressure tank is used. Slepian, who has investigated the whole problem of circuit-breaking quite thoroughly, has recently been laying stress upon the favorable action of the gaseous products in accelerating the recombination of the ions. According to him, the favorable action of a magnetic field consists in deflecting an electric arc at a developing gas bubble towards the surface of the oil, so that the oil is subjected to a more intense decomposition and yields more gas.

On the other hand, such gases are a potential source of danger. Under ordinary operating conditions they may easily become mixed with air and be ignited from the high temperature of the arc; this causes the explosions which have been known to occur. For example, acetylene explodes when it is contained in the air in a concentration of 3 to 52%. These are the so-called lower and upper limits of explosiveness.

Because of the dangers accompanying this decomposition of oil, various ways of preventing it have been sought. One possibility is to use non-inflammable liquids in place of oils. Chlorine derivatives of hydrocarbons, such as carbon tetrachloride  $\text{CCl}_4$ , are not inflammable and are occasionally used. A disadvantage of such dielectrics is the considerable formation of scum in the form of free carbon particles, and also the formation of hydrochloric acid,  $\text{HCl}$ . The latter is very harmful to metal parts in the presence of traces of water. Moreover, such substances evaporate quite readily and often have to be replenished. In the so-called expansion breaker water is used

instead of oil. Owing to an adiabatic cooling of the water vapor in consequence of its expansion, condensation centers are formed which precipitate the ions, thus extinguishing the arc.

A substantially new principle in the manufacture of circuit-breakers is the application of high-pressure gases in place of liquids. A gas under high pressure behaves similarly to a liquid in some respects; we are therefore justified in going into this question here to some extent. It has been explained above that even gases formed from oil are in one respect favorable. Consequently, there ought to be a possibility of extinguishing an electric arc with compressed air. The danger of an explosion would thereby be completely removed. Since the mean free path in a compressed gas has been considerably reduced, although not to the same extent as in a liquid, the action of such a gas should be similar to that of a liquid. It is known that the dielectric strength of a gas increases approximately as the pressure. A similar property should exist also in regard to extinguishing an electric arc.

In the construction so far actually used in practice (the so-called compressed-air circuit-breaker), use is made of gases in motion. Because of this motion the charge carriers are mechanically removed from the space occupied by the arc. It is also possible to extinguish an arc by a purely static gas pressure, this principle having been protected by several patents. The surmise that a static air pressure may be sufficient follows from the known observation that the so-called arc characteristic (voltage as a function of current) is affected by the gas pressure. The higher the pressure, the higher is the voltage for a given current.

A favorable effect of gas pressure may be illustrated by the following experiment made by the author: An air-tight chamber contained a suitable spark-gap 2 mm in width, and in this gap a spark was allowed to pass by applying an over-voltage. Simultaneously an alternating voltage of

6 kV effective value was applied between the electrodes, so that an arc followed the spark. Thus the phenomenon was the same as when the contacts of a circuit-breaker are separated. The arc current could be regulated at will by means of a water resistance in series. The following quantities

were measured: the current, the artificial pressure maintained in the chamber, and, by means of an oscillograph, the number of cycles necessary to extinguish the arc. The gas used was nitrogen.

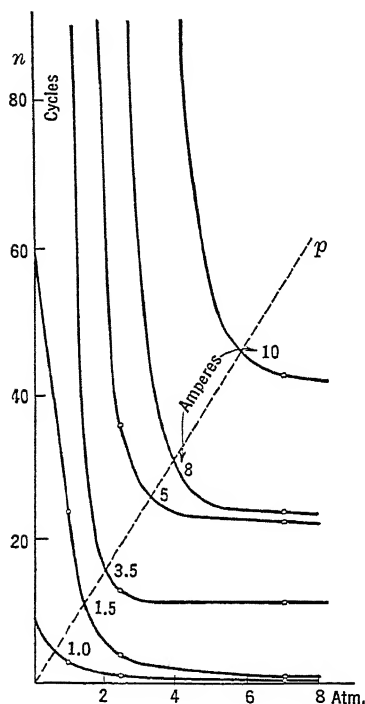


FIG. 56. Number of Cycles ( $n$ ) of Duration of an Arc as a Function of Extinguishing Pressure (the Parameter of Each Curve is the Current in Amperes).

The results of these tests are shown in Fig. 56. Each curve has been plotted for a particular constant value of the current in amperes, and it gives the number of cycles during which the arc "hangs on" as a function of the gas pressure. It will be seen that all the curves rise rapidly when the pressure has been reduced below a certain limit; the arc then lasts for a long time. With higher pressures the arc is easily extinguished. The straight line  $p$  passes through the critical points of the individual curves. The

abscissas of the corresponding points of intersection give values of pressure beyond which, at the corresponding values of current, an arc is promptly extinguished. For a 2-mm gap and an applied voltage of 6 kV effective value, the limiting pressure is 1.5 atmospheres for 1.5 amperes, 5.8 atmospheres for 10 amperes, and so forth; it thus

increases less rapidly than the value of the current. The experiment shows clearly the effect upon the arc of increased pressure, and leads to the conclusion that oil may advantageously be replaced by a compressed gas. The experiment also throws some light on the action of an oil; it is only necessary to extend the curves to the corresponding density. We cannot go into a more detailed theory of arc extinction here.

*Summary.*—The function of a dielectric in a high-voltage circuit-breaker consists in extinguishing the arc, partly by withdrawing some heat from the electrodes and partly by effecting a reduction in the magnitude of the current. Of particular importance is the viscosity of the oil, especially at lower temperatures. Each interruption of a circuit decomposes some oil. The gaseous products of decomposition act favorably, because of their high pressure, but they may easily cause an explosion. This danger may be avoided by using a non-inflammable liquid, for example  $\text{CCl}_4$ . Dense gases (that is, gases under high pressure) also interrupt an arc, for example, by a blast action in a compressed-air circuit-breaker. An experiment is cited showing that a high-pressure gas is also statically effective, considerably reducing the duration of an arc.

### 18. Control Devices for Television and for Sound Films.

—As the last application of liquid dielectrics in electrical engineering we shall describe some practical uses of the Kerr cell. The general problem is to vary the intensity of a beam of light in exceedingly rapid succession, the changes in the intensity to correspond to the fluctuations of an electric current. Such a process may be called electrical control of light.

In television the principle is as follows: a scanned picture, by reflection or absorption, causes variations in the intensity of a beam of light, which, falling upon a photoelectric cell, modulates the transmitted high-frequency waves by means of photoelectric currents. The high-

frequency currents received at the other end are rectified, and then the fluctuations of the current must be transformed into the corresponding fluctuations of a beam of light. Such a control of the beam permits its use photographically or directly for the formation of an image by scanning a photographic plate or a piece of ground glass. Thus in television light control is used in the process of reproduction.

In making a sound film, sound waves are first received on a microphone which converts them into fluctuations of an electric current. Then comes a photoelectric control by means of which corresponding fluctuations of light are produced near the edge of the film, synchronously with the picture being taken. In reproducing the film, a beam of light passes through the edge of the film and affects a photoelectric cell; the currents so generated, after amplification, operate a loud speaker. Thus in this application light control is necessary in the technique of production.

However, the principle of operation is identical in both cases. Various methods have been proposed; until a few years ago, the best consisted of using vibrations of a string excited electromagnetically by fluctuations in a current; the string controlled the effect of a beam of light by screening it off to a variable extent.

This method was by no means sufficiently free from inertia to satisfy the strict requirements. For example, in television the image must be scanned about 20 times per second. A picture of 10 by 10 cm, with an elementary area of 1 mm<sup>2</sup>, has 10<sup>4</sup> such elements, so that  $2 \times 10^5$  vision elements must be transmitted per second. Thus the string would have to adjust itself constantly within less than  $5 \times 10^{-6}$  sec, which is a requirement that can hardly be fulfilled.

On the other hand, a Kerr cell is practically free from inertia and therefore satisfies all the requirements. Continuing the exposition in Section 10, we shall now show how a Kerr cell may be used for light control.

It has been shown that some dielectric liquids, when subjected in a condenser to a field intensity  $E$ , become double-refracting. Let the refractive index of the ordinary beam (oscillation normal to the field intensity) be  $n_0$ , and the maximum value of that of the extraordinary ray (oscillation parallel to the field intensity) be  $n_e$ . The factor  $n_e$  is always greater than  $n_0$ , and the difference  $n_e - n_0$  is given by equation (26). The coefficient of  $E^2$  is denoted by  $K$ ; then

$$(n_e - n_0)/n = KE^2$$

It is customary to work with another constant, a factor  $B$  in place of  $K$ , where

$$B = K/\lambda$$

$\lambda$  being the wavelength in the medium without the electric field. We then have

$$(n_e - n_0)/(n\lambda) = BE^2$$

or

$$1/[(n/n_e)\lambda] - 1/[(n/n_0)\lambda] = BE^2$$

The denominators on the left-hand side give the respective wavelengths of the extraordinary and the ordinary ray of light. Their reciprocals give the numbers of wavelengths per centimeter. Thus the left-hand side of the equation gives the phase difference between the two beams when both travel 1 cm. In other words, if both rays begin a path in the same phase, then after 1 cm the phases of the two will differ by  $BE^2$  wavelengths. If the length of the path be  $l$  centimeters, the phase difference  $\phi$  will be  $BlE^2$ , so that

$$\phi = BlE^2 \quad (35)$$

In this manner, if the path covered by the beam, the distance between the condenser plates, the voltage, and the factor  $B$  are known, the phase difference  $\phi$  between the beams oscillating normally and parallel to the direction of the electric field may be computed.

We shall now show the result of a phase difference, in the sense of equation (35), when a linearly polarized beam of light is sent through a Kerr cell. In Fig. 57, let  $A$  and  $B$  be the electrodes of a cell, and  $E$  the field intensity. Let some linearly polarized light be sent through the cell

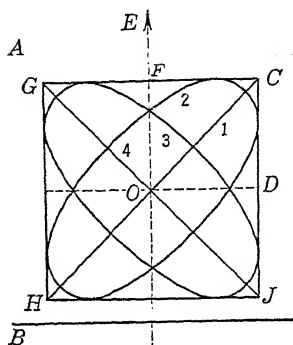


FIG. 57. Plane Polarized Light in a Doubly-refracting Liquid.

in a direction perpendicular to that of the plane of the paper and hence parallel to the plates  $A$  and  $B$ ; let the electric oscillations be in the direction 1, at an angle of  $45^\circ$  to the direction  $E$ . Let the waves' amplitude  $r = OC$ . This amplitude may be resolved into two perpendicular components,  $OD$  and  $OF$ , which originally swing in phase with each other. However,  $OD$  oscillates in a direction normal to  $E$  and therefore is an ordinary

beam, whereas  $OF$  oscillates in the direction of  $E$  and consequently is an extraordinary beam with a maximum of refractive index.

By purely geometric reasoning it may be demonstrated that when there is a phase displacement between  $OD$  and  $OF$ , the resultant of the two is no longer a straight-line oscillation, but an ellipse inscribed within the square  $CGHJ$ , with its principal axes always in the direction of the two diagonals. Originally the ellipse is spread out as shown at 2; it then becomes flat, as shown at 3, contracts into the straight line 4, and so forth. Its form varies periodically with the increasing phase angle  $\phi$ . Let the semi-axis perpendicular to 1 be called  $r'$ ; we then have

$$r' = r \sin \pi \phi \quad (36)$$

The vector  $r'$  reaches its maximum for  $\phi = 0.5$ ; the emerging light is then again linearly polarized, except that the direction of polarization has been rotated by  $90^\circ$ . The



intermediate stages are known as elliptically polarized, because the electric vector of the beam of light describes an ellipse.

Substituting the value of  $\phi$  in equation (36), we obtain

$$r' = r \sin (\pi B l E^2)$$

so that  $r'$  varies periodically with increasing field intensity. The problem is to utilize optically the amplitude  $r'$ . Then the problem of light control ( $r'$  as a function of  $E$ ) is solved.

A suitable arrangement is shown in Fig. 58.  $L$  is a point source of light, and  $a$  is a convex lens which converges the beam and sends it through the Kerr cell  $c$ ; the beam is perpendicular to the direction of the electric field,

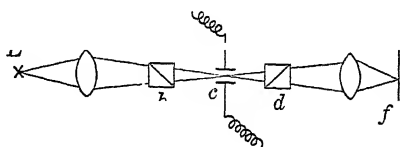


FIG. 58. The Optical System of a Kerr Cell.

as in Fig. 57. A Nicol prism  $b$  allows only rays with a definite direction of electric oscillation to pass through it;  $b$  is turned about its longitudinal axis until the direction of oscillation forms an angle of  $45^\circ$  with the plane of the paper. The emerging ray passes through the lens  $e$  and converges upon the screen  $f$ . At  $d$  a second Nicol prism is mounted and so set that it allows only those oscillations to pass which are normal to those of the prism  $b$ ; thus  $d$  is an indicator of the component  $r'$ . When no electric field is applied across the cell,  $r'$  is equal to zero, and the screen remains dark. With increasing field intensity,  $r'$  increases according to equation (36), and the field of vision on the screen becomes more and more bright. The intensity of light in terms of energy being proportional to the square of its amplitude, we have

$$I' = I \sin^2(\pi B l E^2) \quad (37)$$

where  $I'$  denotes the intensity of the light passing through the prism  $d$ , and  $I$  the intensity of the beam after absorp-

tion in  $b$  and in the lenses,  $I$  being smaller than one-half of the original light intensity from the source.

A portion of a curve for  $I'$  as a function of  $E$  is shown in Fig. 59. It is known as the voltage-light characteristic of the Kerr cell. The first maximum, corresponding to  $\phi = 0.5$ , is included in this section. The marked part is approximately a straight line and is the working range of the curve. The initial voltage is so chosen that the field intensity comes out equal to  $E_0$ ; a modulation voltage is superimposed upon it, with a view to obtaining the greatest possible differences in the light intensity on the screen.

As is mentioned in Section 10,  $B$  varies within wide limits with the wavelength of the light used. Therefore the characteristic shown in Fig. 59 reproduces not equation

(37), but (if white light is used) a sum of many similar equations with different values of the constant  $B$ . Therefore the exact form of the characteristic is somewhat variable for different substances, in accordance with the variability of  $B$  with  $\lambda$ .

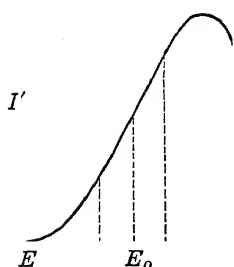


FIG. 59. A Characteristic of a Kerr Cell.

The effect is extraordinarily rapid, as may be seen from Section 9, in which the time constant of dipole rotation was discussed. It was shown there that  $\tau$  is of the order of magnitude of  $10^{-10}$  sec, so that for the present requirements of television a Kerr cell may be considered as being practically without inertia.

With a given wavelength the constant  $B$  varies largely with the chemical nature of the liquid in the Kerr cell. For practical applications the highest possible value of  $B$  is desirable. Nitrobenzene, whose average Kerr constant  $B$  is approximately equal to  $4 \times 10^{-5}$ , satisfies this condition. Nitro-groups are particularly effective in raising this constant; halogen groups are not so effective. With isomeric

substances the para-compounds have the highest Kerr constant.

Moreover,  $B$  depends considerably upon the temperature, as may be seen from equation (26). This variation is particularly pronounced with dipole compounds. For nitrobenzene  $B$  decreases in the ratio of 4 : 3 between  $6^\circ$  and  $25^\circ$  C, exactly in accordance with the theory. This characteristic is very disturbing in application to sound films, because the Kerr effect decreases in an undesirable manner with increasing room temperature. This reduces the average light intensity, which corresponds to  $E_0$ , and has to be compensated for by choosing a higher value of the initial voltage. Still more undesirable is the property of nitrobenzene to freeze at  $5.8^\circ$  C, which makes it impossible to make records at low temperatures. For such purposes nitrotoluol is used, with the average value of the Kerr constant at about  $2.6 \times 10^{-5}$ ; this substance has a lower melting point.

The degree of purity of the fluid used is of very great importance. Impurities are disturbing in several respects. First, they may cause undesirable field distortions in the Kerr cell. Second, they reduce the value of the Kerr constant itself. Third, they cause a high conductivity, with the result that at a desired voltage the conduction current becomes disturbingly high. Fourth, a lower breakdown strength is also disturbing. For these reasons, the liquid to be used is repeatedly distilled in vacuum, then purified electrically to remove moisture and other possible admixtures, and finally sealed in vacuum. Nickel is recommended as material for the electrodes. By purifying the liquid its conductivity is decreased from  $2 \times 10^{-8}$  mho/cm to  $1 \times 10^{-10}$  mho/cm, and the dielectric strength is increased to  $1.5 \times 10^5$  volts/cm.

Such cells usually have a gap of approximately 0.15 mm, and the average voltage is about 1000 volts ( $7 \times 10^4$  V/cm). In order to use a larger total flux of light it is advisable to connect several condensers of this sort in parallel both

electrically and optically; the same voltage is then sufficient and the available light is better utilized.

*Summary.*—The Kerr cell is the best light-control device for the purposes of television and sound film. In such a cell an ordinary and an extraordinary beam of light acquire a phase difference which is proportional to the square of the applied voltage. The intensity of the outgoing light may then be controlled electrically by means of a second Nicol prism. Liquids with high values of Kerr constant  $B$ , such as nitro-benzol, are best. Control is effected practically without inertia. The disturbing factors are a high conductivity of the liquid used and the variations of the Kerr constant with temperature. A thoroughgoing purification of the liquid is indispensable.

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